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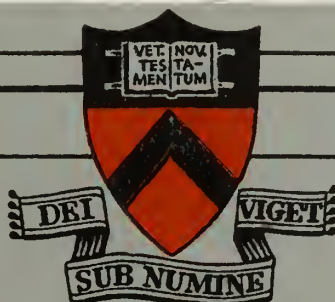
THE INTERACTION OF CLAY MINERALS WITH SOME  
UNUSUAL ORGANIC LIQUIDS

by

Richard E. Andrews, LTJG CEC USN

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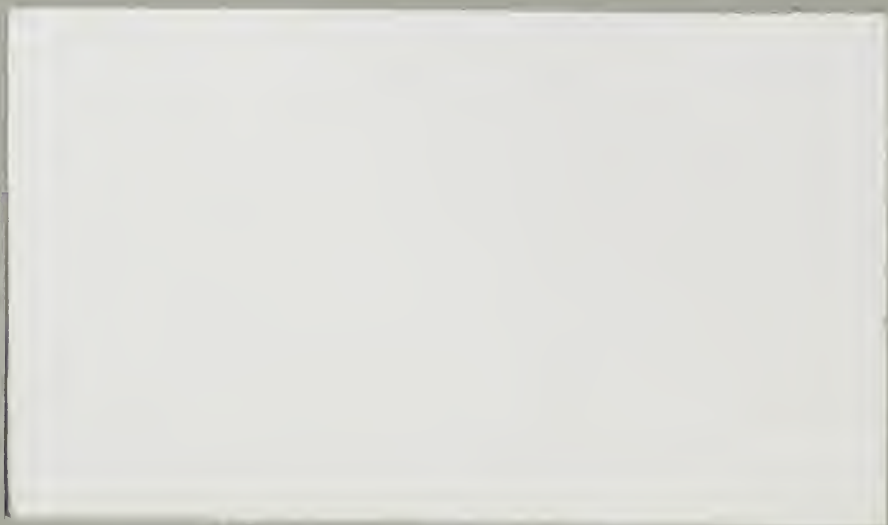
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Submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering from Princeton University, 1966.

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## INTRODUCTION

This investigation was primarily motivated by the newly discovered strange properties of a long known organic liquid. The liquid is dimethyl sulfoxide (DMSO) and it was highly publicized in the mid 1960's as a medical miracle drug. The properties of DMSO which make it a miracle drug are its penetrating ability due to its strong interaction with protein-like molecules and water. This allows the DMSO to pass through the skin and be distributed throughout the body very rapidly. Since it is also a solvent it was used in clinical tests to carry other drugs and medications throughout the body. It also has some pain killing qualities by itself and was thus used as a treatment for arthritis, rheumatism and other similar afflictions. Similarly in the agricultural field, DMSO was applied to plants and trees to permeate them with both pesticides and nutrients.

An analogy was therefore made between the human body and the soil-water system and initially it was hoped to direct the work toward investigations of the use of DMSO as a carrier of chemicals in soil stabilization. It was thought from the analogy that better penetration would occur in the soil system, using DMSO as the agent or carrier, rather than water.

After consideration of this it was decided that prior to research in the use of DMSO in soil stabilization, some basic research must be conducted in the interaction of DMSO with various clay minerals. The work of Waidelich [20] in 1957 which investigated the interaction of clay minerals and water and organic liquids was used as a point of departure for this investigation.





The investigation used three clay minerals of different structure and was aimed at obtaining a comparison of the clay - DMSO interaction and the clay-water interaction. Some tests were also conducted employing another organic liquid, Dimethyl Formamide (DMF) but the full series of tests were not run due to constraints on the safe use of the liquid and the type of tests conducted.



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I. MATERIALS USED IN THE INVESTIGATIONA. Liquids

The liquids used in this investigation were water, Dimethyl Sulfoxide (DMSO), and for a limited number of tests, Dimethyl Formamide (DMF). These are all polar liquids, i.e., the center of charge of the positive charges does not coincide with the center of charge of the negative charges, consequently a dipole moment is formed. If the dipole moment is caused by the structure of the molecule itself, it is called a permanent dipole. If it is caused by the separation of positive and negative charges resulting from a strong electric field superimposed on the molecule, it is an induced dipole. Water, DMSO, and DMF all have permanent dipoles.

Table 1 lists some of the significant physical properties of the liquids used, and a discussion of each of the liquids follows.

TABLE 1

	H <sub>2</sub> O	DMSO	DMF
Formula	H <sub>2</sub> O	SO(CH <sub>3</sub> ) <sub>2</sub>	HCON(CH <sub>3</sub> ) <sub>2</sub>
Specific Gravity at 20°C/20°C	.99823	1.1008	.950 at 20°C/15.6°C
Molecular Weight	18.00	78.13	73.09
Melting Point	0.0°C	18.45°C	-61.0°C
Boiling Point at 760 MM Hg	100.0°C	189.0°C	153.0°C
Specific Heat Cal/gm	1.0	.47 at 29.4°C	.5 at 20°C
Surface Tension Dynes/CM	72.75	42.85	35.2
Viscosity-CP at 25°C	.894	1.98	.802
Refractive Index	1.33 at 20°C	1.4783 at 20°C	1.4269 at 25°C
Dielectric Constant	80 at 20°C	48.9 at 20°C	26.6 at 25°C
Dipole Moment-Deybes	1.89	3.9	3.85

[Ref. 8,11,16,18,2,10]



## 1. Water

Water, although one of the most well-known and abundant of natural occurring materials, is a peculiar substance. As pointed out by Winterkorn [21,22], water at a molecular weight of 18 is one of the lightest molecules known to Chemistry, and, in comparison with similar hydrides on the same vertical or horizontal lines of the periodic chart, should be a gas at normal pressures and temperatures instead of a liquid. Even as a liquid, water possesses some properties characteristic of the solid state, as exemplified for instance by its high specific heat.

The peculiarities of water have been traced to the structure of the water molecule, and the fact that water has a permanent dipole, with a dipole moment of approximately  $1.87 \times 10^{-18}$  ESU. The water molecule which can be considered approximately spherical has a radius of about  $1.38 \text{ \AA}$ . This small molecule size along with the large dipole moment produces a strong, directed interaction of adjoining water molecules and consequently a highly associated structure. The interaction between the water molecules prevents a close packing of the molecules and the associated structure can be termed "loose" [15,21]. A representation of the water molecule is shown in Fig. 1.

Water being a polar solvent follows the general rule that polar solvents have high dielectric constants. Water, at  $18^\circ\text{C}$ , has a dielectric constant of about 81. High dielectric constants insure that the electrostatic interactions between centers of charge (anions and cations) are minimized or greatly reduced, consequently dissolved anions and cations do not aggregate. This is accomplished by the ions being surrounded by the oriented water







FIGURE 1

MOLECULAR STRUCTURE OF WATER MOLECULE



dipoles so that opposite charges are as close to each other as possible. This phenomenon is known as solvation. It should be noted that in water, both anions and cations are solvated and shielded from each other.

## 2. Dimethyl Sulfoxide (DMSO)

Dimethyl sulfoxide, chemical formula  $\text{SO}(\text{CH}_3)_2$ , is a solvent chemically related to acetone ( $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$ ) and was first synthesized in 1867 by German scientists. It is now obtained by oxidizing liqnin-derived dimethyl sulfide. It is a colorless liquid completely miscible with water and extremely hygroscopic. It has a slightly bitter taste and practically no odor. [5]

DMSO has, since 1961, been hailed as a medical "wonder drug", while still only in the clinical test stage. Due to its strong interaction with both water and protein-like molecules, it has the ability to pass rapidly through the body. It has therefore been used therapeutically as a pain-killer to treat bursitis, arthritis, burns, and sprained joints. It has received equal acclaim as a vehicle to carry other medicines and drugs such as anti-biotics into the human system. In this connection, scientists have proposed use of DMSO to carry oxygen in the form of hydrogen peroxide to the heart muscle for treatment of massive heart attacks.

However, in November, 1965, all clinical tests were halted and the drug was withdrawn from use by the Food and Drug Administration. This action was taken because changes in the eyes of animals undergoing tests with DMSO were observed. The changes involved alterations of the refractive index of the animals eyes [13,14,15].



In view of the withdrawal of the drug from medical test programs, every precaution was taken in the laboratory. Neoprene gloves were worn whenever the DMSO was handled, and, to the maximum extent feasible, the tests and handling of the DMSO were conducted under ventilation hoods.

### 3. Dimethyl Formamide - DMF

Dimethyl Formamide, chemical formula  $\text{HCON}(\text{CH}_3)_2$ , is a very powerful solvent and has many industrial applications. It is a colorless, mobile liquid with faint amine odor and is completely miscible with water and organic solvents. It is a good carrier solvent for gases and is often used wherever a solvent with a low rate of evaporation is required.

DMF vapors are harmful and may be adsorbed through the skin. It is highly irritating to the skin, eyes, and mucuous membranes. Liver injury has resulted in experimental animals through prolonged inhalation of 100 ppm [11].

Due to the demonstrated toxicity of DMF, precautions were taken in the laboratory and only tests were conducted which allowed even minimal opportunity for the release of vapors.

### DMSO and DMF Discussion

Both DMSO and DMF are acidic solvents. Both solvents are polar. The dielectric constant is 48.9 at 20°C for DMSO and 26.6 at 25°C for DMF. Although not as high as the dielectric constant of water (78.5 at 25°C), the dielectric constant of both DMSO and DMF is indicative of polar liquids [8,16].

The molecular size of the DMSO molecule is about  $6.2 \text{ \AA}$  in the long dimension and  $4.0 \text{ \AA}$  in the short dimension. The mole-



cular size of the DMF is approximately  $6.4 \text{ \AA}$  in the long dimension and  $3.5 \text{ \AA}$  in the short. Structurally, the molecules are as shown in Fig. 2. Thus both are structurally different and larger than the water molecule. Consequently, while there is still considerable structure in both the DMSO and DMF due to polarity, it is looser and the forces between molecules are smaller. The structure is therefore less disturbed by the introduction of foreign molecules and hence these molecules dissolve more readily in the DMSO or DMF than in water.

Another significant difference between water on one hand and DMSO or DMF on the other involves solvation. As previously indicated, both anions and cations are surrounded in water by the oriented water dipoles and consequently both anions and cations are solvated and shielded. The hydrogen bonding between the anions and the water dipole is very strong, since the positive charge on the small hydrogen atoms of the water molecule can come closer to an anion than can the positive charge on atoms other than hydrogen. In DMF or DMSO, since the positive center is on an atom other than hydrogen, the interaction with the anion is significantly weaker and the anions are not shielded. This, in essence, means that DMF or DMSO shield and solvate only cations and the anions are effectively free. Figs. 3 and 4 are illustrations of the different reactions of water and DMSO or DMF with anions and cations.

The dipole moment of DMF is 3.85 Deybe units [10]. The dipole moment of DMSO, as furnished by the manufacturer, is 3.9 Deybe units, as compared to about 1.87 Deybe units of water. It should be remembered that the dielectric constant of water





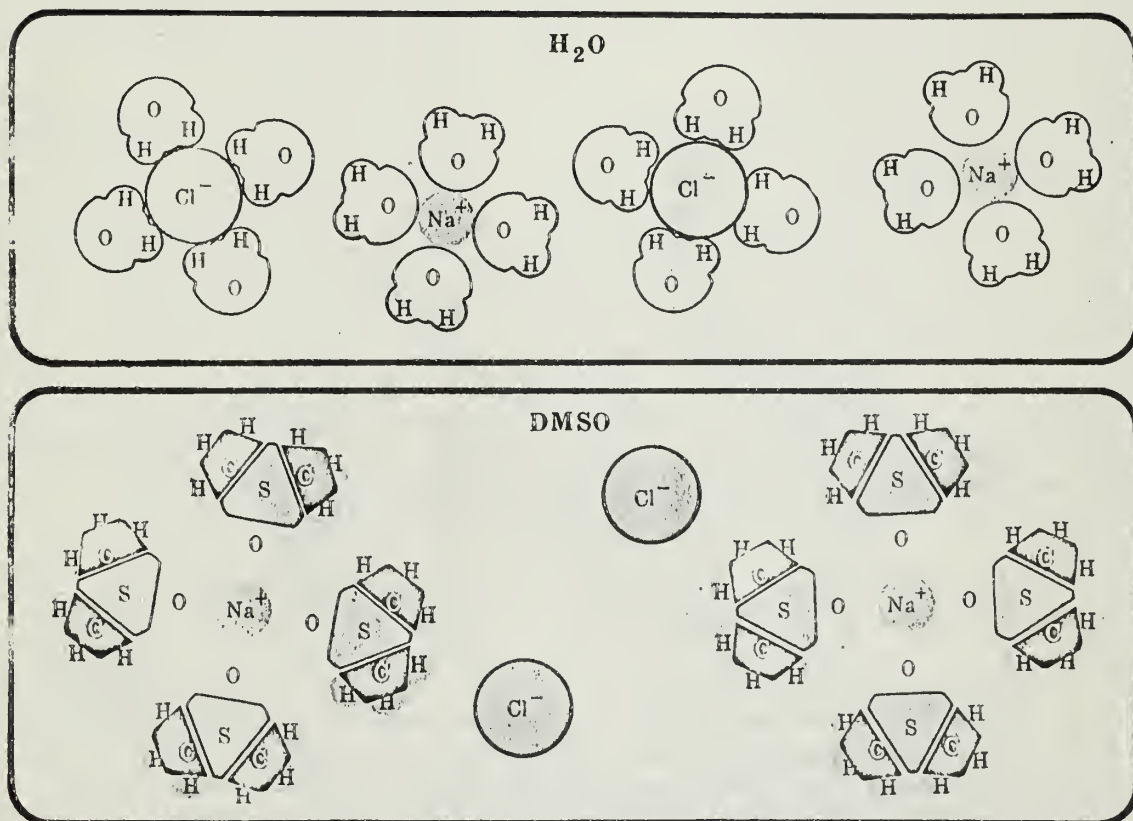


MOLECULAR STRUCTURE OF DMSO MOLECULE



MOLECULAR STRUCTURE OF DMF MOLECULE





*Fig. 1. The nature of solution varies with the solvent. In water, both anions and cations are solvated and shielded from each other; in DMF and DMSO only the cation is so shielded. In a truly inert solvent, all ions would be free.*

(Figure 1, Ref 15)

FIGURE 3



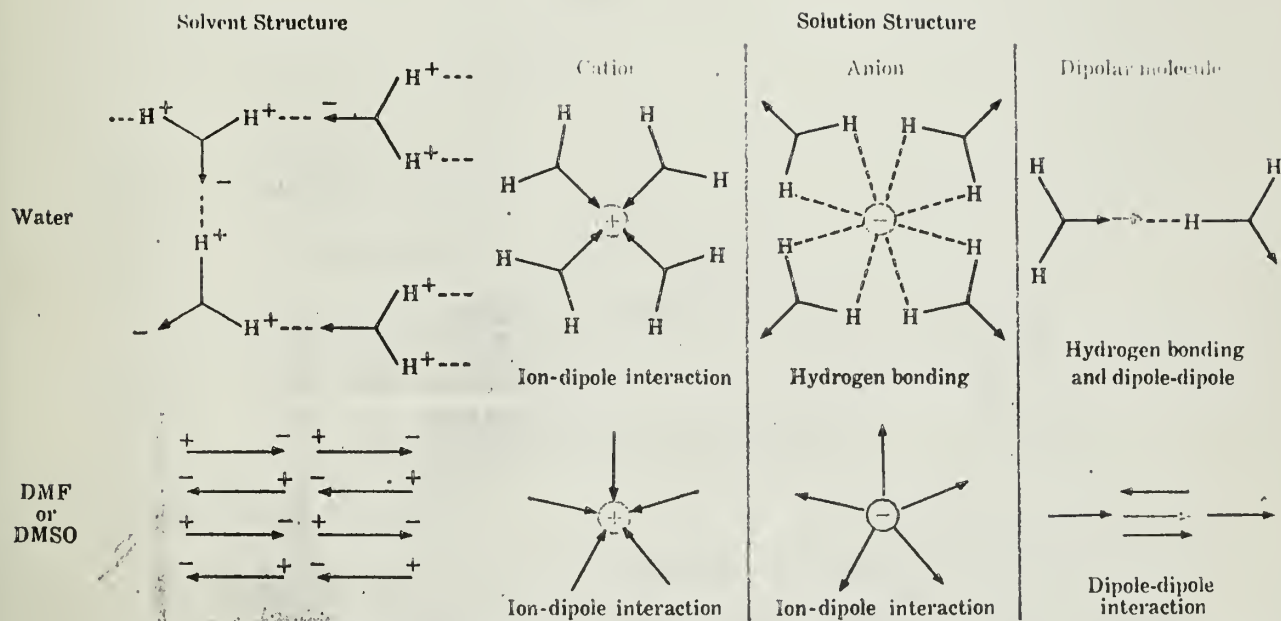


Fig. 2 Differences in solvent structure result from different interactions between their molecules. This also affects solution processes. In diagram, arrow represents a dipolar molecule, its head the negative end and its tail the positive end. Dipoles tend to orient themselves so that opposite charges are as close to each other as possible (i.e., energy is minimized); this is solvation.

(Figure 2, Ref 15)



is about 80 and of DMSO about 45. This seeming inconsistency supports the generalization stated by Pimental and McLellan [16] that the dielectric constant and dipole moment do not increase together.

This is immediately shown by Debye's equation [22] where:

$$\frac{D-1}{D+1} \frac{M}{\rho} = \frac{4\pi A}{3} \left( \alpha + \frac{u^2}{3KT} \right) \quad \text{in which}$$

D = dielectric constant

M = molecular weight

$\rho$  = density

A = Avogadro number

$\alpha$  = polarizability of molecules

u = permanent dipole moment

K = Boltzmann constant

T = Absolute temperature

## B. The Clay Minerals

Three clay minerals of different structures were selected to be used in the tests with the polar liquids. The minerals were kaolinite with a rather strongly bonded (hydrogen bonds) layered structure, attapulgite with its distinctive hollow tube structure, and montmorillonite with its expanding lattice structure. In their interaction with water, the montmorillonite is the most active, the kaolinite the least active, and the attapulgite occupies a position somewhere in between.

### 1. Attapulgite

The name attapulgite was first given in 1935 by De Lapparent to a fibrous clay mineral he encountered in Fuller's earth from a number of locations including Attapulgis, Georgia.





The structure of Attapulgite was studied in detail by Bradley and consists of double silica chains running parallel to the fiber axis. The silica unit can be considered an  $\text{Si}_2\text{O}_3$  layer in which the Si atoms occur in strips alternately on both sides of the oxygen. Between successive  $\text{Si}_2\text{O}_3$  layers are octahedral strips containing  $\text{M}_g$  and Al which hold the sheets together. The alternation in the silicon causes similar alternations in the octahedral strip so that open channels of fixed dimensions run parallel to the chain. Water molecules fill these channels, half lying adjacent to the octahedral strips and the other half taking definite positions in the channels. The channel cross sections are about  $3.8 \times 6.3 \text{ \AA}$  [4,9].

Grim [3] visualizes the structure of Attapulgite as consisting of a bundle of lath-shaped units tied together at the long edges in a regular fashion. The exterior of the bundle would have a plateau and channel appearance and the interior would consist of an alternation of solid laths and elongated channels at rectangular cross section.

Fig. 5 is an atomic model of Attapulgite and Fig. 6 is a schematic representation of the structure.

The chemical composition of Attapulgite, as postulated by Bradley, is  $(\text{H}_2\text{O})_4(\text{OH})_2 \text{M}_{g5}\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ . Aluminum may replace some of the magnesium.

The attapulgite used in the investigations was supplied by the Minerals and Chemicals Division of Minerals and Chemicals, Philipp Corporation, Menlo Park, New Jersey, and came from Attapulgis, Georgia. The type was Attagel 30, with an average particle size (equivalent spherical diameter) of 0.12 microns.



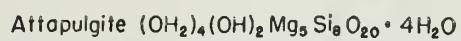
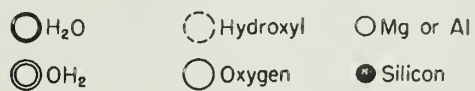
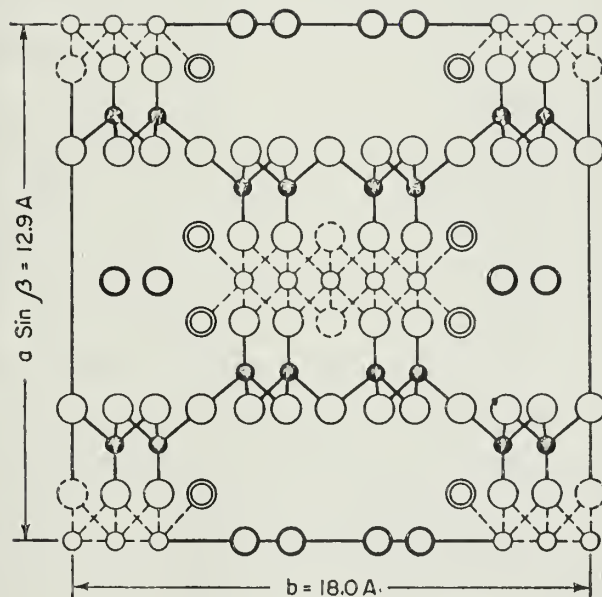


*Fig. 41* Atomic model of attapulgite.

(Figure 41, Ref 9)

FIGURE 5





Schematic presentation of the structure of attapulgite, after Bradley.

(Figure 19, Ref 4)

FIGURE 6



The actual chemical composition of Attagel 30, as furnished by the producer is listed in Table 2. X-ray diffraction of Attagel 30 confirms this.

TABLE 2

Chemical Composition of Attapulgitite	
Silicon ( $\text{SiO}_2$ )	68.0%
Aluminum ( $\text{Al}_2\text{O}_3$ )	12.0%
Magnesium ( $\text{MgO}$ )	10.5%
Iron ( $\text{Fe}_2\text{O}_3$ )	5.0%
Calcium ( $\text{CaO}$ )	1.7%
Phosphorus ( $\text{P}_2\text{O}_5$ )	1.0%
Potassium ( $\text{K}_2\text{O}$ )	1.0%
Titanium ( $\text{TiO}_2$ )	0.7%
Trace Elements	0.1%

[Ref. 12]

## 2. Kaolinite

Kaolinite is the mineral that characterizes most kaolins, which as indicated by Ross and [4] is "the rock mass which is composed essentially of a clay material that is low in iron and usually white or mostly white in color." The word Kaolin is a corruption of the Chinese word "Kauling", the name of a hill in China where the clay was obtained centuries ago for the manufacture of porcelain.

The structure of Kaolinite is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that a common interface is formed by one of the planes of the octahedral sheet and the tips of the silica tetrahedrons. The plane dimensions (a and b) of the tetrahedral and





octahedral sheets are closely similar thus allowing the formation of composite octahedral-tetrahedral layers. These composite layers are continuous in the a and b directions and stack one above the other in the c (normal) direction. The thickness of one of the composite octahedral-tetrahedral layers is approximately 7.1 Å. In the stacking of these composite layers, the superposition of the oxygen and hydroxyl planes in adjacent layers causes the composite layers to be held fairly tightly by hydrogen bonding [3,9]. Figure 7 is a diagrammatic sketch which illustrates the structure of the composite octahedral-tetrahedral layers.

The structural formula for Kaolinite is  $(\text{OH})_8 \text{Si}_4 \text{Al}_4 \text{O}_{10}$ . There are very very few substitutions for aluminum in nature. The theoretical composition expressed in oxides is  $\text{SiO}_2$  - 46.54%;  $\text{Al}_2\text{O}_3$  - 39.50%; and  $\text{H}_2\text{O}$  - 13.96%.

The Kaolinite used in the investigations was supplied by the United Clay Mines Corporation, Trenton, New Jersey, and was a Georgia sedimentary kaolin. It is a coarse grained clay with an average particle size (equivalent spherical diameter) of 3 microns.

X-ray diffraction of the Kaolinite indicate a well-crystallized Kaolinite with some disorder along the b axis.

### 3. Western Bentonite (Montmorillonite)

The word bentonite was first applied in 1898 by Knight to a highly colloidal plastic clay found in the cretaceous beds of Wyoming. Bentonite has the ability of swelling to several times its original volume when placed in water and also has the ability of forming thixotropic gels with water even when the amount of clay is relatively small.



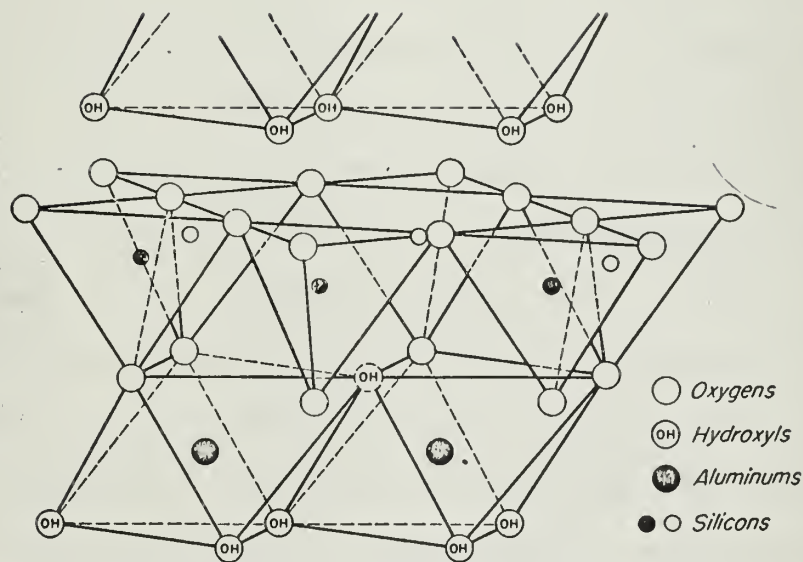


FIG. 4. Diagrammatic sketch of the structure of the kaolinite layer, after Gruner.<sup>4</sup>

(Figure 4, Ref 4)

FIGURE 7



The Western Bentonite used was produced by the American Colloid Company, New York and was Number 200, Voclay. The company could not supply the average particle size. X-ray diffraction of the Western Bentonite showed it was basically a sodium montmorillonite.

The structure of montmorillonite was proposed by Hoffmann, Endell, and Wilm (1933), Marshall (1933), and Hendricks (1942). Essentially they conceptualize montmorillonite as being composed of two silica tetrahedral sheets with a central alumina octahedral sheet. The tetrahedral sheet combines with the octahedral sheet in such a way that the tips of the tetrahedrons and one of the hydroxyl layers of the octahedral sheet form a common interface. The silica-alumina-silica layers are continuous in the *a* and *b* directions and are stacked one above the other in the *c* direction. In this type of stacking, the interface of the adjacent composite layers consists of oxygen planes. This results in a very weak bond and a cleavage between the adjacent composite layers. Water or other polar liquids can enter this cleavage and cause an expansion in the *c* direction. The expansion may be many molecular layers thick, thus the *c*-axis dimension is not fixed but varies from about  $9.3 \text{ \AA}$  or the thickness of a composite layer upward. With sodium as the exchangeable cation between composite layers, under ordinary conditions, there is one molecular water layer and a *c*-axis spacing of approximately  $12.5 \text{ \AA}$  [3,9]. A schematic diagram of the montmorillonite structure is shown in Figure 8 and a diagrammatic edge view, which better indicates the swelling between composite layers, is shown in Figure 9.



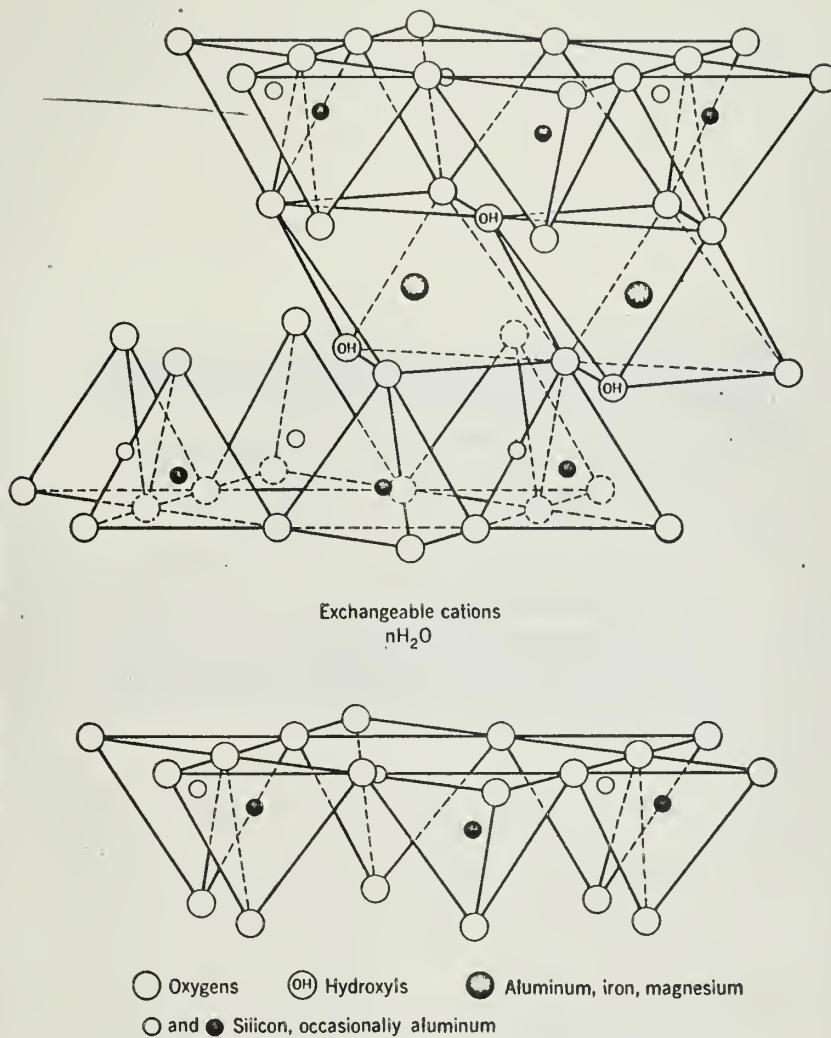
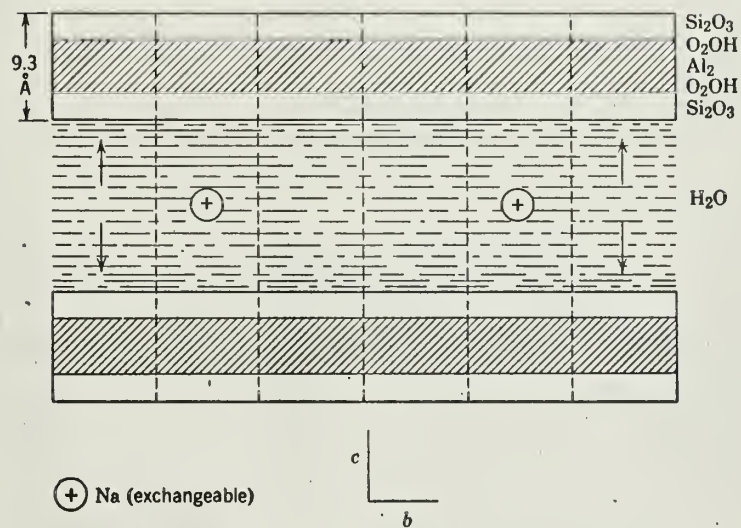


FIG. 2-7. Diagrammatic sketch of the structure of montmorillonite, according to Hofmann, Endell, and Wilm (1933); Marshall (1935); and Hendricks (1942).

(Figure 2-7, Ref 3)







**Fig. 35** Diagrammatic edge view of montmorillonite.

(Figure 35, Ref 9)

FIGURE 9



The theoretical structural formula for the montmorillonite is  $(OH)_4 Si_8 Al_4 O_{20} n$  (interlayer)  $H_2O$ . The theoretical composition without the interlayer (cleavage) material is  $SiO_2$  - 66.7%;  $Al_2 O_3$  - 28.3%;  $H_2O$  - 5.0%. Montmorillonite always differs from the above theoretical formula because of substitutions for the silicon in the tetrahedral sheets and for the aluminum in the octahedral sheets. Montmorillonites normally tend to occur in equidimensional, extremely thin flake-shaped units, although in some instances the units are elongated and are lath or needle shaped [3].

#### 4. Clay Minerals Base Exchange Capacity

The base exchange capacity of the clay minerals used in the tests in milliequivalents per 100 grams is as follows:

Kaolinite	3 - 15
Attapulgite	20 - 30
Montmorillonite	80 -150

This represents the milliequivalents of cations adsorbed on the surface of 100 grams of clay particles and exchangeable for other cations that are introduced into the system.

The discovery that soils have the power of exchanging cations with solutions containing other cations results from many observations dating back to antiquity. For example, it has been known for centuries that liquid manures are decolorized and deodorized when filtered through soils. The first person who systematically studied cation exchange was Thompson, starting in 1845. J. F. Way in 1850, showed cation exchange was restricted to the clay fractions in the soil. Since then many scientists have studied the aspects of the exchange reaction.



The base exchange capacity is dependent on the electric and geometric pattern of the clay surface structure, the size and valence of the cations and the thickness of the adsorbed moisture film [4,22].



## II. DESCRIPTION OF EXPERIMENTS

### A. Atterberg Limits

The Atterberg limits or consistency limits tests are the well known tests to determine the boundary between the solid, the semi-solid, the plastic and the liquid states of fine grained cohesive soil samples. Particularly these tests have been very useful in describing the character of the fines in the soil material. These tests are also useful in describing the cohesion or bonding characteristics of the soil and in this respect relate to the shear strength of the material. This is true because the shear strength of the soils with large clay content is dependent mainly upon the cohesive or binding forces of the clay particles as a function of the water content and is relatively independent of the interparticle friction forces in the material. The phrase relatively independent of interparticle friction forces is used because it has been shown particularly by Dos Santos that granulometry of a soil material has an important effect on the consistency properties.

The three boundaries between the liquid and plastic states the plastic and semi solid states and the semi-solid and solid states are respectively described by the liquid, plastic and shrinkage limits of the soil materials.

The only limits found in this test were the liquid limit and plastic limit of the three clays with water and DMSO. The shrinkage limit was not determined because of the nature of the DMSO and clay mixtures upon oven drying. Whereas the water and clay mixtures form a relatively stable cast upon drying, the





DMSO and clay mixture would form a weak cast which was unstable and would disintegrate into a powdery mass if disturbed.

The liquid and plastic limit tests were conducted in accordance with ASTM standard test D 423 - 61T and D 424 - 59 [1] with only slight modification, this being that the soil liquid mixture was allowed to stand overnight in a dessicator before testing to insure that the soil liquid interaction had reached an equilibrium state. Also because of the unknown toxicity of the DMSO liquid, neoprene gloves were worn during the plastic limit testing of DMSO clay mixtures. The samples were allowed to remain in a drying oven at a temperature of 107°C for twenty-four hours or until there was no further weight change of the sample.

Table 3 illustrates the results of these tests. The liquid and plastic limits are represented in the standard manner as the percentage of liquid per dry weight of the sample. The plasticity index is also shown representing the difference between the liquid and plastic limit or the moisture range in which the soil has plastic properties.

TABLE 3

Atterberg Limits

Test Liquid Soil	Liquid Limit		Plastic Limit		Plasticity Index	
	H <sub>2</sub> O	DMSO	H <sub>2</sub> O	DMSO	H <sub>2</sub> O	DMSO
Kaolinite	62	105	33	50	29	55
Attapulгите	291	309	110	155	181	154
Western Bent.	506	140	55	80	451	60



## B. Specific Gravity

"Specific gravity is the ratio of the weight in air of a given material at a stated temperature to the weight in air of an equal volume of distilled water at a stated temperature." [1] In the case of a soil, the specific gravity relates to only the solid phase and in the metric system is also a measure of the density of the material. In a soil the specific gravity also is an average of all the specific gravities of the separate soil particles.

It was shown by E. W. Russell [17] around 1934 that the specific gravity is not only dependent upon the nature of the solid material but is also dependent upon the liquid used and the interaction between the soil particles and the liquid. This interaction is extremely important in the case of clay minerals and provides a good indicator of the activity of the clay. Specifically it was found by Mr. Russell that "(1) No evidence could be obtained of interaction between clays and non-polar liquids. (2) Interaction took place in all the polar liquids examined." [17] Further work has been done concerning the interaction of different polar liquids with clay minerals by W. C. Waidelich at Princeton University in 1957 [20].

The specific gravity tests were conducted in accordance with ASTM test designation D 854 - 58 with certain modifications due to the unusual character of the DMSO liquid and the high activity of the clay soil. The major modification to the test was that the clays were oven dried before addition of the two liquids. The reason this was done was to reduce the interaction between the DMSO and the bound water in the soil. Since the DMSO is



extremely hygroscopic and since the air dry moisture contents of the more active clays were in the neighborhood of ten (10%) by weight of the soil it was important to have as little moisture in the soil as possible so as to reduce any interference by the water at the soil - DMSO interface. Also after addition of the liquid to the clay sample, the sample was allowed to stand overnight to allow the soil liquid interaction to reach an equilibrium state.

The following procedure was used in the test.

1. Small weighing bottles of approximately 50 ml. capacity were weighed empty to the nearest thousandth of a gram on a Will Corporation balance accurate to  $\pm 0.1$  mg.
2. The bottles were calibrated at different temperatures using a constant temperature bath. Half the bottles were calibrated using DMSO and half with water. The bottles were placed in an evacuated dessicator at about 115 mm. of mercury after filling to insure the removal of entrapped air in the liquid, before being placed in the temperature bath. A curve was then drawn giving the weight of the bottle and liquid in the desired temperature range.
3. The bottles were then emptied, dried, filled with a quantity of oven dried soil and weighed after the soil had cooled.
4. Then the bottles were filled about half way with liquid and allowed to stand overnight.
5. The bottles were then placed in a dessicator and the dessicator was evacuated by a HYVAC oil vacuum pump to a pressure of about 115 mm. of mercury. The bottles



were spun gently and tapped at intervals to insure the removal of all entrapped air. The bottles remained in dessicator under vacuum overnight.

6. The bottles were then removed from the dessicator, filled completely with liquid and the mixture was weighed. The specific gravity could then be calculated.

The temperature of the main supply of liquids and the temperature within the dessicator never varied more than  $\pm 1.0^{\circ}\text{C}$ .

It is important to insure that all entrapped air be removed from the liquid soil mixture. If this is not done carefully the weight of the mixture will be less than it should be and the calculated specific gravity will be incorrect and smaller than it would be if no air bubbles were entrapped.

Since the specific gravity of the DMSO was greater than that of water (sp. gr. DMSO is  $\approx 1.095$  at  $27.5^{\circ}\text{C}$ ) the calculations of the specific gravity of the soil in the DMSO had to be modified by using the exact volume of the DMSO displaced rather than the weight of the DMSO.

Careful records of the temperature of the liquid were taken during the tests so that the specific gravities found could be adjusted and standardized at a temperature of  $20^{\circ}\text{C}$ . This temperature is the temperature at which specific gravities are reported following the procedure of ASTM D 854.

The results of the specific gravity test are given in Table 4.





TABLE 4

## Specific Gravity

Soil	Liquid	
	H <sub>2</sub> O	DMSO
Kaolinite	2.6137	2.5924
Attapulgate	2.6126	2.5674
Western Bent.	2.5136	2.9237

C. Dietert Compaction

The Dietert Compaction Apparatus was a device first developed by the American Foundrymen's Association for the compaction testing of foundry sands. It was later adopted for use in the Laboratory of Messrs. Soil Mechanics, Ltd., London, for determining the optimum moisture content of soils. The apparatus was also compared by Soil Mechanics Ltd. with the more standard laboratory compaction method developed by Proctor around 1933 [7]. Good correlation was determined between the two methods.

The original Dietert Compaction apparatus consisted essentially of an 18-pound weight mounted on a slide which could be lifted a distance of two inches and then dropped by a hand operated cam. Attached to the bottom end of the slide was a metal rod with a 2-inch diameter foot at the bottom. This foot fitted inside a two-inch diameter cylinder under the weight and resting on the base of the apparatus. The soil sample, approximately 150 gms., was placed in the sample cylinder and the cam operated so that the force of the falling weight would be transmitted to the soil through the foot and compaction effected in this way. Originally ten blows were given one side



of the sample, then the cylinder inverted and ten blows given on the other side. However, research by Soil Mechanics Ltd. showed that better correlation could be obtained with the Proctor test using a total of only five blows on the sample. Once the cylinder was compacted the weight and length of the pat could be measured and its density determined. Further by oven drying the sample the moisture content could be determined at any density. One hundred fifty grams of soil was used in the tests because it gave a sample length of approximately two inches [7].

A modified Dietert Compaction apparatus was used in determining optimum moisture contents for this report because it has certain advantages over the Proctor method. In particular smaller amounts of material, both liquid and soil, could be used, about 1/10 as much as would be needed in the standard Proctor. Secondly and even more important, mixing could be effected much more easily. It was extremely important since tests were being made on some highly active clay minerals that there be complete mixing of the liquid and soil.

The modified Dietert apparatus (Fig. 10) was different from the originally developed one in the distance the weight fell, the method of dropping the weight and the sample cylinder. In the modified compactor the weight was raised by hand a distance of  $2\frac{7}{8}$  inches and then dropped. The sample cylinder is changed (Fig. 11) by placing a fork (A) between the sample cylinder (B) and the base (C). The weight is dropped twice with the fork in place. Then the fork is removed and the weight is dropped an additional three times. What this does in effect



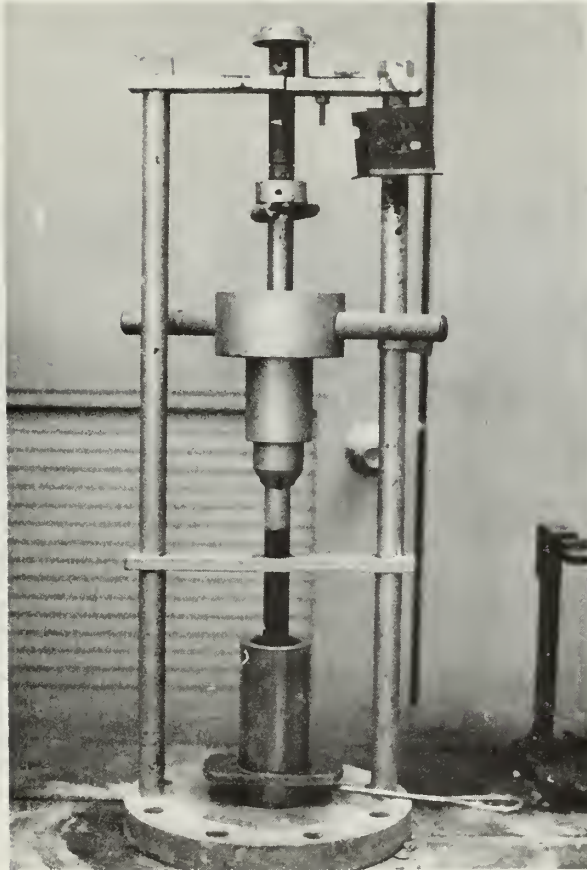


FIGURE 10

DIERTERT TESTING APPARATUS



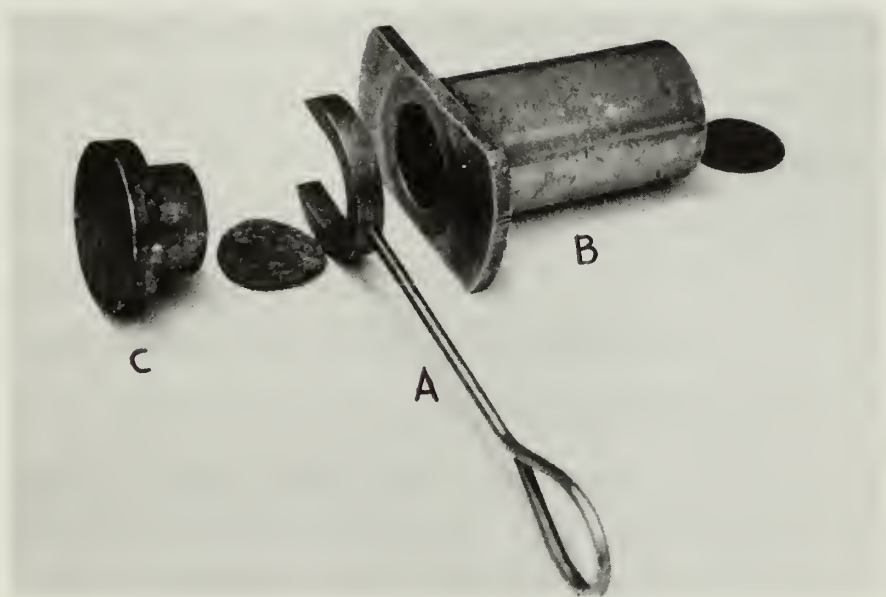


FIGURE 11  
MODIFIED SAMPLE CYLINDER  
FOR DIETERT TEST





is reduce any friction between the cylinder and the sample during the final three blows of compaction. The cylinder is not restrained from moving with the sample as the sample is compacted in the final stage so no compaction energy is lost sliding the sample down the inside of the cylinder.

The test was further modified by oven drying soils before mixing them with the DMSO liquid. This was done again to reduce the interaction between the DMSO liquid and any bound water. In each case the oven dry soil was mixed with the liquid (usually about 6 samples of the same soil and liquid were mixed with about 10% difference by weight of liquid added) and the samples were allowed to stand in a dessicator overnight to reach equilibrium before being tested.

The optimum moisture contents for compaction found in this test were a good indicator of the different interaction which took place with our two liquids and the soils.

The results of these compaction tests are plotted as sample length vs. liquid content on the following pages and table 5 gives the optimum (liquid) content for compaction of the three soils.

TABLE 5

Optimum Moisture Contents From Modified  
Dietert Test

Liquid		
Soil	H <sub>2</sub> O	DMSO
Kaolinite	28	40
Attapulgate	49	36
Western Bent.	~ 50 *	~ 76 #



SAMPLE LENGTH - INCHES

2.3

2.2

2.1

2.0

1.9

10

20

30

40

PERCENT LIQUID

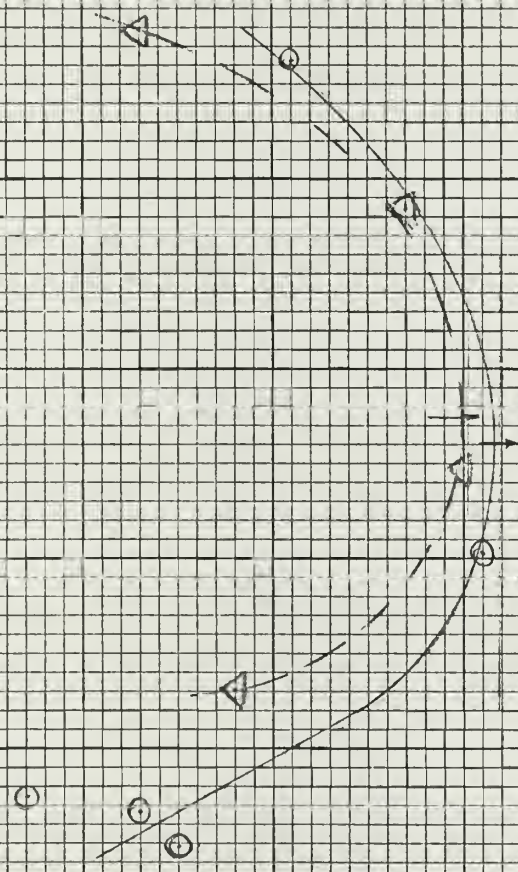
DIRECT COMPACTION TEST

140g AIR-DRY

KAOLINITE AND H<sub>2</sub>O

○ RUN 1

△ RUN 2







2.2

2.1

2.0

1.9

1.8

1.7

LENGTH - INCHES

SAMPLE

## DIETERT COMPACTION TEST

60g AIR-DRY

ATTAPULGITE AND H<sub>2</sub>O

-O RUN 1

-A RUN 2

-B RUN 3

80

70

60

50

40

30

PERCENT LIQUID





2.5

2.4

2.3

2.2

2.1

2.0

SAMPLE LENGTH - INCHES

⊙

△

⊙

⊙

△

⊙

△

△

△

△

DIETER COMPACTION TEST

140g AIR-DRY

BENTONITE AND H<sub>2</sub>O

⊙ RUN 1

△ RUN 2

30

20

10

0

40

PERCENT LIQUID





2.7

2.6

2.5

2.4

2.3

20

30

40

50

SAMPLE LENGTH - INCHES

PERCENT LIQUID

47

⊙ ⊙

△

△

⊕

⊙

△

⊕

⊕

DIETERI COMPACTION TEST

140 g OVEN DRY

KAOLINITE AND DMSO

⊙ RUN 1

△ RUN 2





2.5

2.4

2.3

2.2

2.1

2.0

1.9

2.0

30

40

50

60

70

80

SAMPLE LENGTH - INCHES

PERCENT LIQUID

CWC

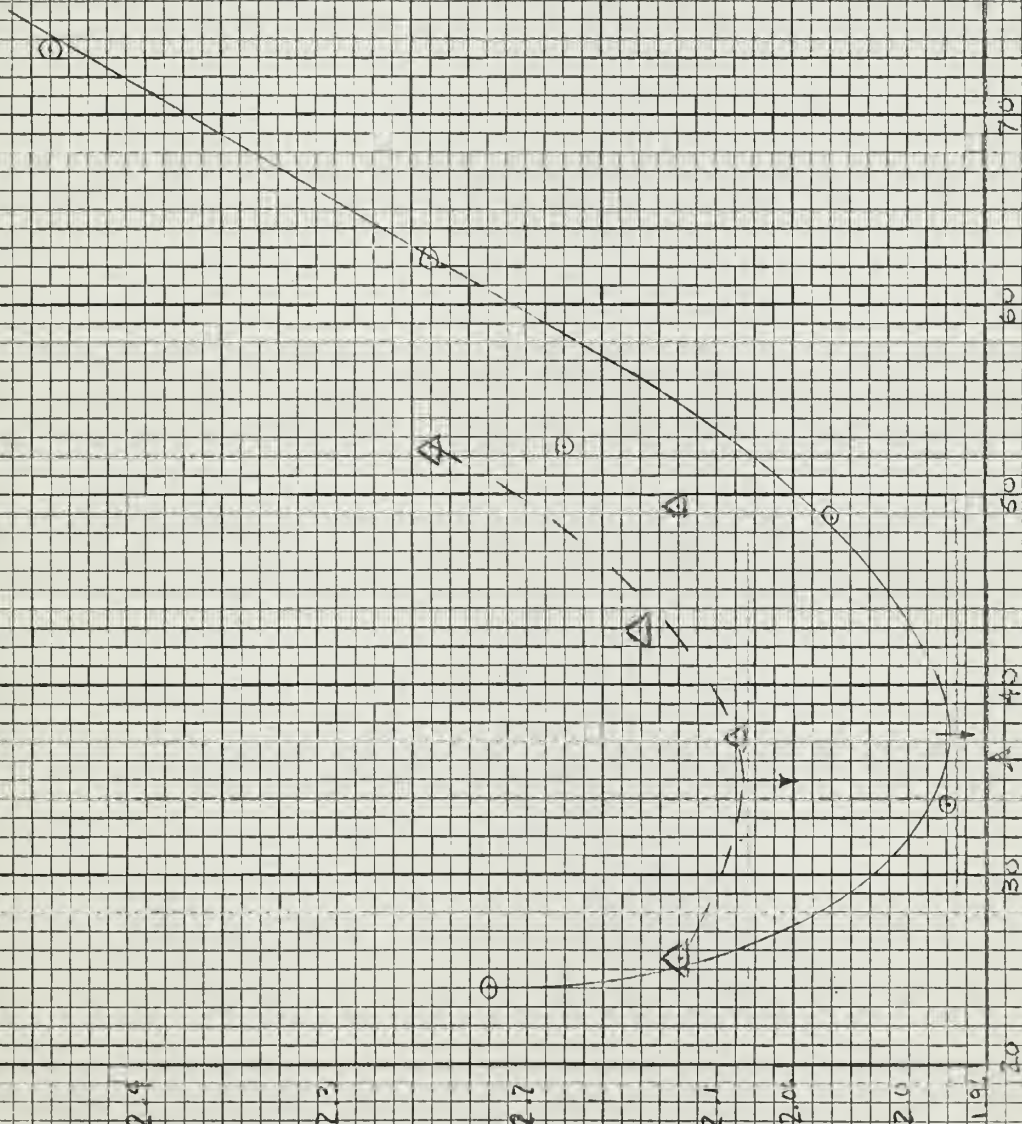
DIETERI COMPACTION TEST

OVEN-DRY 60.3

ATTAPULGITE AND DMSO

O RUN 1

A RUN 2







# DIETERT COMPACTION TEST

70g OVEN-DRY \*

WESTERN BENTONITE AND

DMSO

△ RUN 1

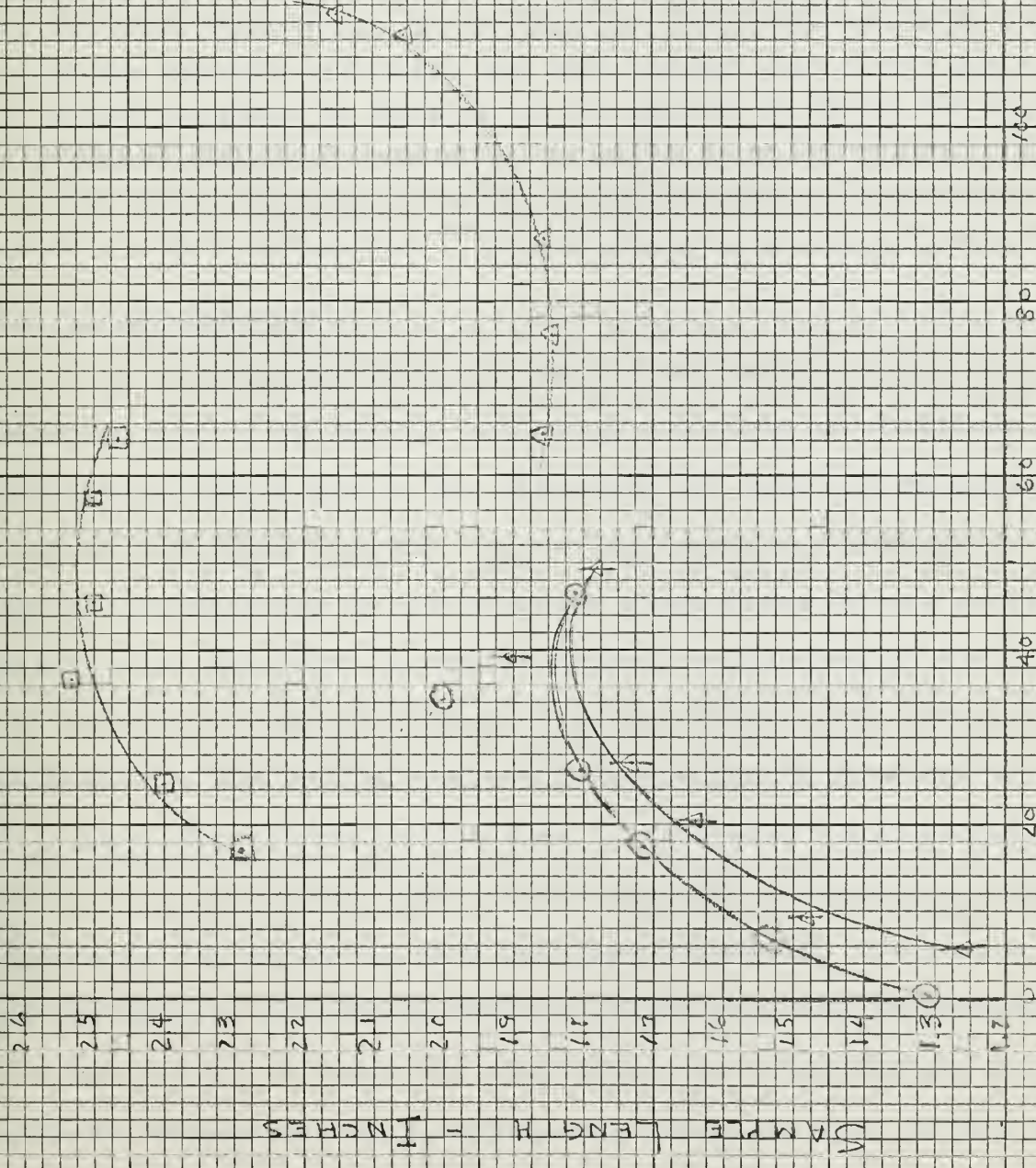
○ RUN 2

□ RUN 3

△ RUN 4

\* NOTE

RUN 3 WAS MADE USING 90g



PERCENT LIQUID



Table 5 - Continued

- \* In the case of Western Bentonite and  $H_2O$ , the sample length (density decreased) consistently from moisture content of 10% on up, indicating tremendous swelling with little lubrication. Since the plastic limit is an indication of the satisfaction of the of the major water affinity of the particle, and since this factor is of major importance in determining the optimum liquid content it was decided it was more realistic to represent the OMC as approximately the plastic limit of the soil, rather than the maximum density point.
- # The same comments as above (Western Bentonite and  $H_2O$ ) apply to the Western Bentonite and DMSO except that there was a slight decrease in density of the sample at about 76% liquid content after the continuous increase from 10% on up. See plot sample length vs. moisture content for W.B. and DMSO.

#### D. Liquid Sorption

The liquid sorption test which measures the amount of liquid adsorbed into a particular soil sample affords an excellent yet relatively simple method for observing the swelling mechanism of various soils and liquids. Since the swelling phenomena is not only a function of the electric force field of the colloid but is also dependent on the electrical properties of the liquid, the results of this test should further clarify the interaction between the liquids and soil colloids tested in this study.

Work was actually first done in this area by Winterkorn and Baver around 1933 [23]. They developed a relatively simple apparatus for measuring this swelling phenomena. They also tested the effects of various liquids on the swelling properties of certain clays. Essentially they found that swelling increased with an increasing Si-O<sub>2</sub>-sesquioxide ratio but that it was also





a function of the adsorbed cations in the colloid. They also found that swelling in both polar and non-polar liquids seemed to increase with the increase of the dielectric constant of the liquid. The results of the tests by Winterkorn and Baver are important in evaluating the sorption tests done in this report and further discussion is given in Section III.

The apparatus used in the sorption test was patterned after the one used by Winterkorn and Baver. It consists essentially of a Buchner funnel with a fused in glass filter plate attached to a graduated pipette. The pipette was of capillary size with a capacity of 1 ml. and could be read accurately to the nearest  $\pm 0.001$  ml. The pipette was connected to the Buchner Funnel by a small glass tube (Fig. 12). When the swelling of Bentonite and Attapulgate was measured it was desirable to place a 3-way stopcock attached to a liquid reservoir between the funnel and the pipette (Fig. 13). This modification was necessary because of the high sorption capacity of the two aforementioned soils. The three way stopcock permitted introduction of additional liquid into the pipette while the sorption test was in progress. The top inside diameter of the pipette was level with the top of the glass filter plate so that zero head occurred at this point. It was also desirable to use only a relatively small amount of soil for this test, so sections with a volume of 3 ml. were cut from an old burette. One end of each one of these sections was covered with a fine mesh nylon and a measured quantity of soil was placed in the cut burette. Then the soil was densified by gently tapping the burette section on the table six times. Approximately equal void



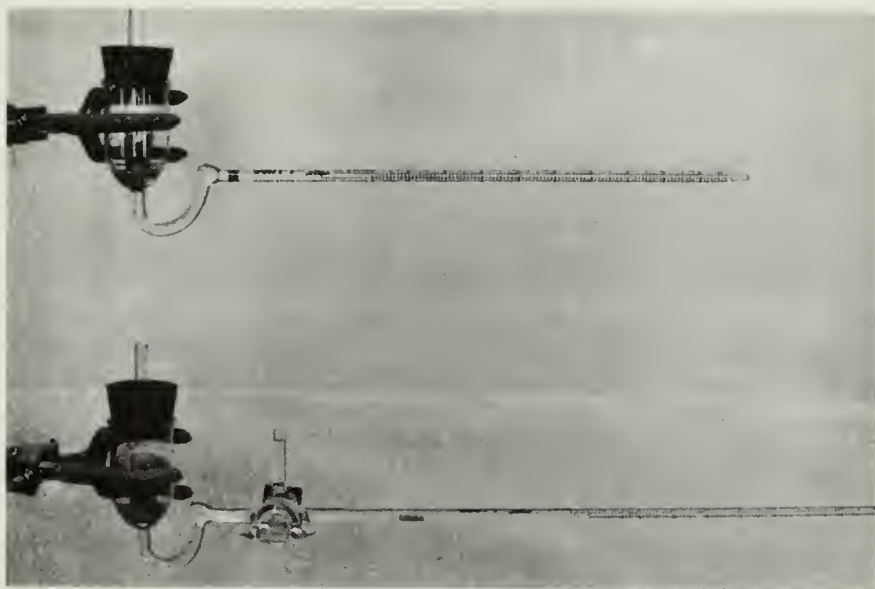


FIGURE 12 & 13  
SORPTION APPARATUS



ratios were obtained in this manner. (The uniform densification was verified by observing that approximately the same volume was filled in the burette sampler by equal weights of the same type soil.) The burette section with the sample was next placed on the glass filter plate in the funnel. The top of the funnel was sealed with a rubber stopper with a capillary tube in it. The capillary tube allowed equal pressure on both surfaces of the liquid but also reduced to negligible any evaporation loss that would occur.

Two test runs were made using six similar apparatus with the three soil types and the liquids DMSO and distilled water. In the first test run 0.5 gm. of Attapulgate, 1.0 grams of Western Bentonite and 1.0 grams of Kaolinite, all air dry, were used in the experiment. The original moisture contents of these samples were approximately 0.05% for Kaolinite, 8.0% for Attapulgate and 10.0% for Western Bentonite. Two samples of each of the soil types were weighed and one of these samples was placed in the sorption apparatus containing DMSO and another in the one containing water. Readings were taken at various time intervals over a period of 2640 minutes. In the second test run the soil was dried over  $P_2O_5$  before being weighed and tested. Water contents after drying for 48 hours for Kaolinite, Attapulgate and Western Bentonite were respectively 0.05%, 7.4%, and 4.9%. Readings for this second run were taken at various intervals over a period of 8640 minutes.

It is logical to assume, that the sorption capacity was linearly proportional to the weight of soil used. Therefore for the sake of comparison of results, since different weights of



soil were used in each test, the test data were multiplied by a corresponding correction factor so the results could be standardized to the amount of liquid adsorbed per 0.5 gm. of soil. The results of the test are illustrated in Tables 6 and 7. The results are also plotted as sorption (ml.)/0.5 gm. of soil vs. the log of time on the following pages.





TABLE 6

Test Run #1 Air Dry Soils

Sorption (ml.) per 0.5 gm. Colloid

Time Minutes	Kaolinite		Attapulgitite		West. Bent.	
	H <sub>2</sub> O	DMSO	H <sub>2</sub> O	DMSO	H <sub>2</sub> O	DMSO
0	.000	.000	.000	.000	.000	.000
1	.018	.042	.265	.072	.034	.128
2	.031	.085	.592	.179	.046	.174
3	.049	.128	.900	.278	.054	.211
4	.105	.164	.999	.370	.059	.240
5	.148	.199	1.111	.470	.065	.264
10	.348	.348	1.273	.892	.084	.348
20	.395	.470	1.354	1.033	.106	.497
30	.398	.480	1.384	1.049	.126	.565
60	.422	.499	1.424	1.060	.181	.652
120	.425	.505	1.454	1.075	.226	.689
180	.428	.507	(176) 1.467	1.085 (209) 1.090	.264 (221) .282	.704 (217) .710
1200	.439		1.578	1.170	.492	.733
1440	.441		1.595	1.178	.520 (1596) .538	.735
2640	.460		(2580) 1.657	1.209	.588	.792

Original Moisture Contents

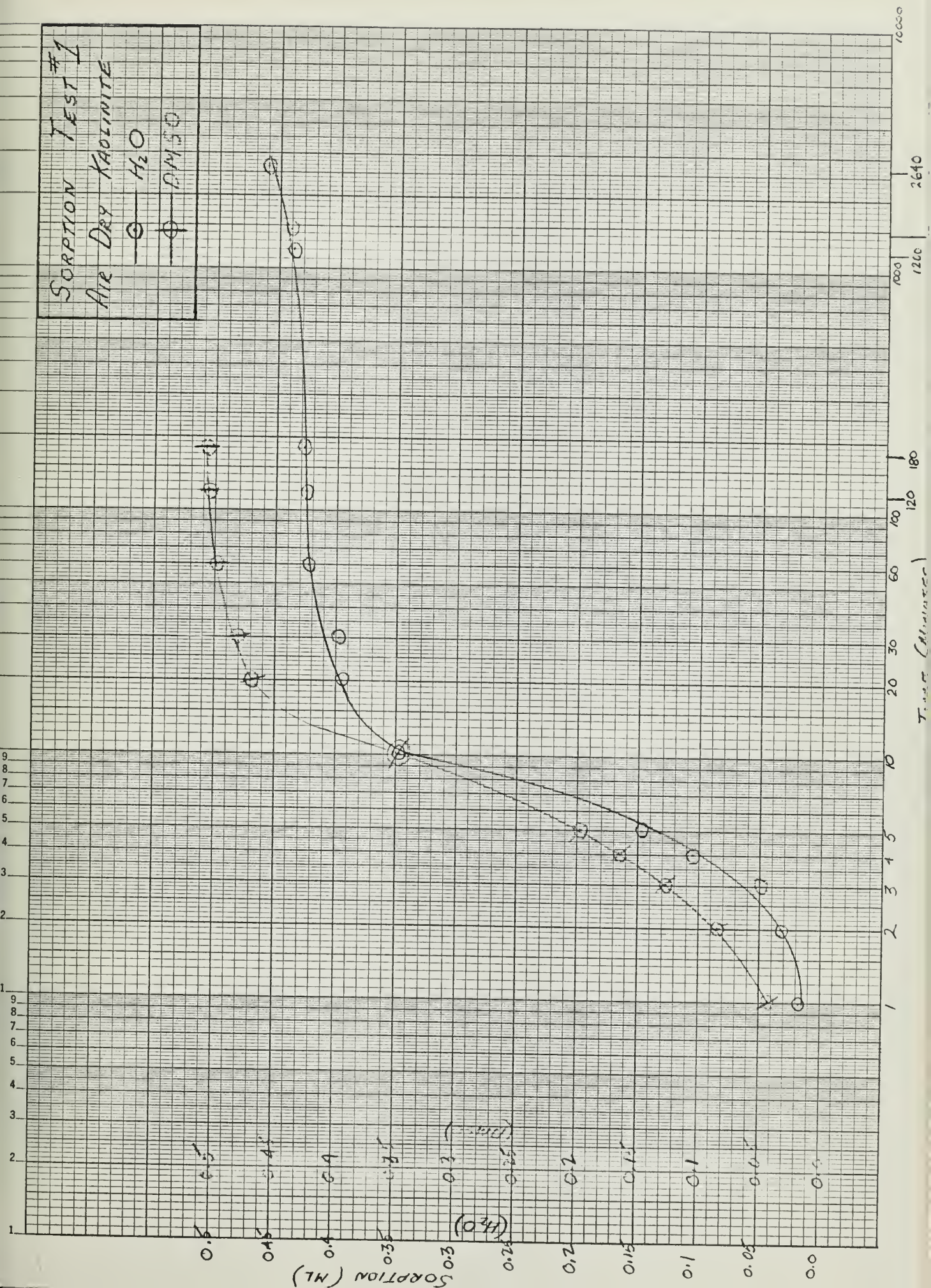
.05%

8%

10%

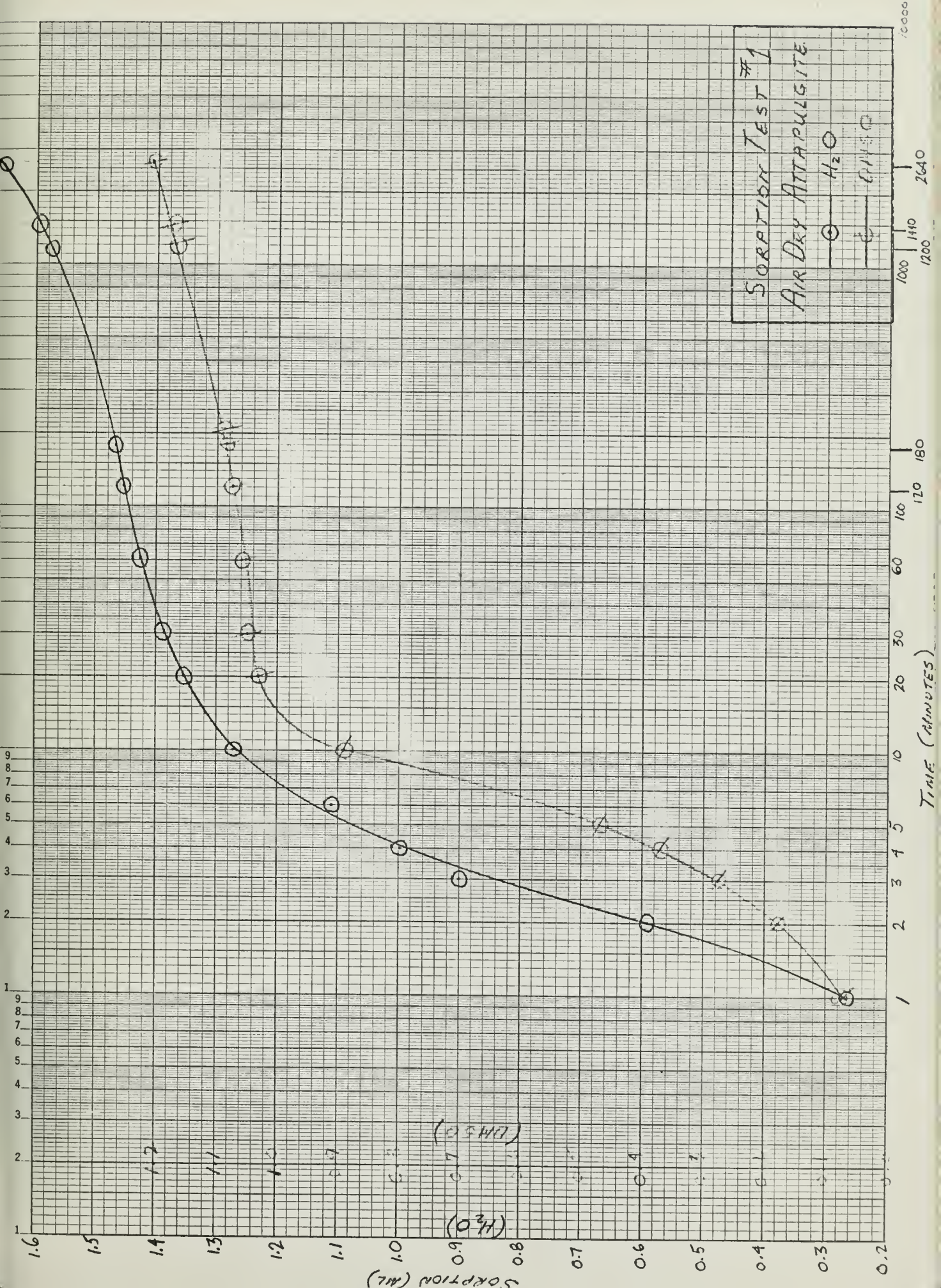


SORPTION TEST #1  
 Air DRY KAOLINITE  
 —○—  $H_2O$   
 —⊕— DMF50













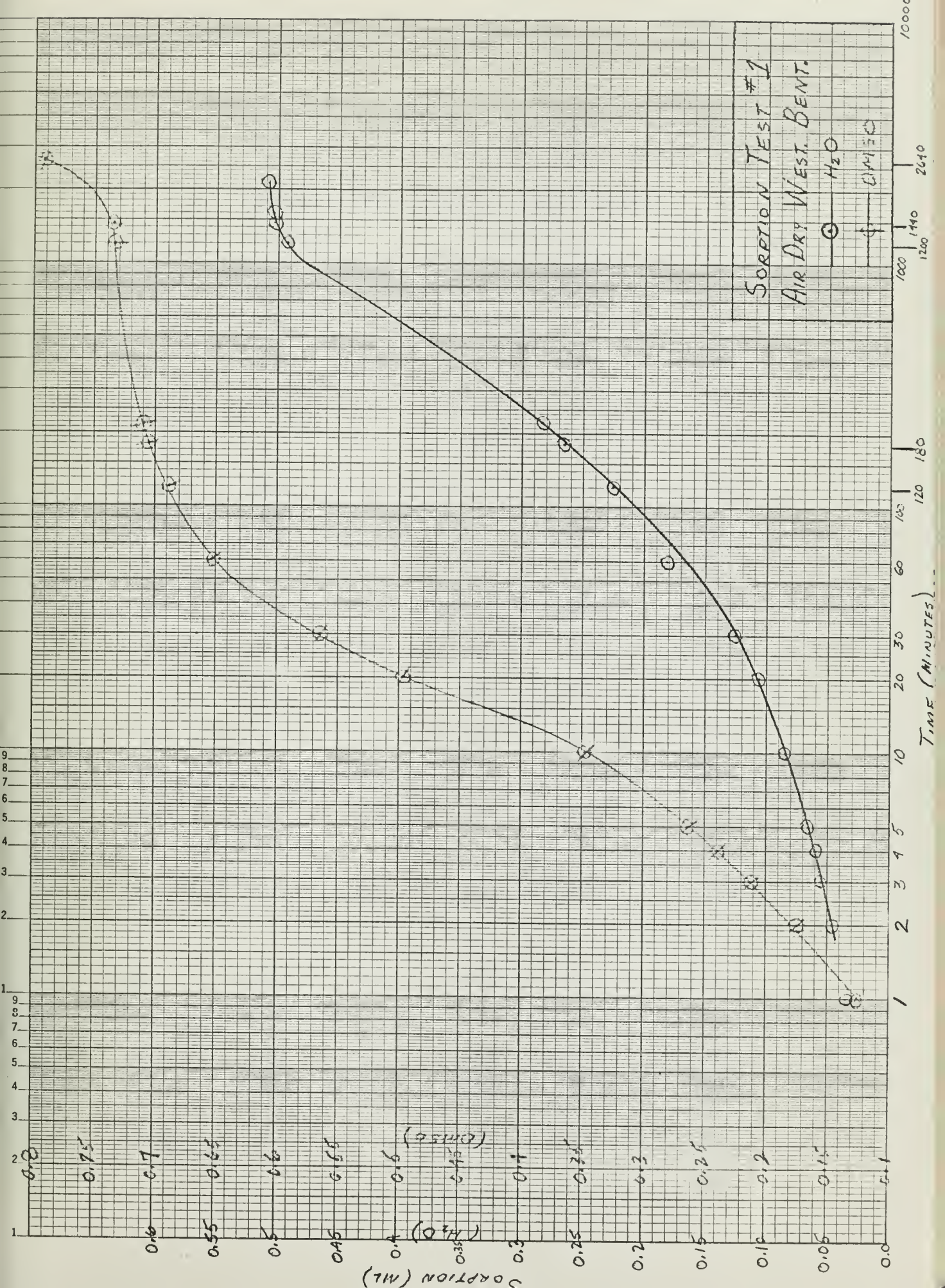






TABLE 7

Test Run #2 Dessicator Dry Soils

Sorption (ml.) per 0.5 gm. Colloid

Time Minutes	Putnam		Attapulgitite		West.Bentonite	
	H <sub>2</sub> O	DMSO	H <sub>2</sub> O	DMSO	H <sub>2</sub> O	DMSO
0	.000	.000	.000	.000	.000	.000
1	.087	.033	.273	.070	.025	.108
2	.165	.065	.574	.164	.043	.154
3.	.227	.094	.860	.285	.052	.194
4	.280	.132	1.0	.409	.060	.226
5	.323	.157	1.1	.520	.069	.255
10	.339	.315	1.209	.821	.091	.352
20	.384	.467	1.262	.880	.112	.490
30	.388	.475	1.300	.890	.125	.601
60	.391	.479	1.320	.945	.152	.667
120	.398	.483	1.355	.956	.194	.704
180	.402	.487	1.370	.970	.217	.718
240	.404	.488	1.380	.980	.239 (325) .265	.724
1320	.432	.514	1.460	1.060	.428	.738
1440	.434	.520	1.464	1.064	.440	.740
2880	.457 (4410) .475	.592 (4410) .652	1.470 (4388) 1.565	1.098 (4388) 1.120	.560 (4399) .652	.744 (4399) .75
8640	.514	.727	1.665	1.152	.857	.758

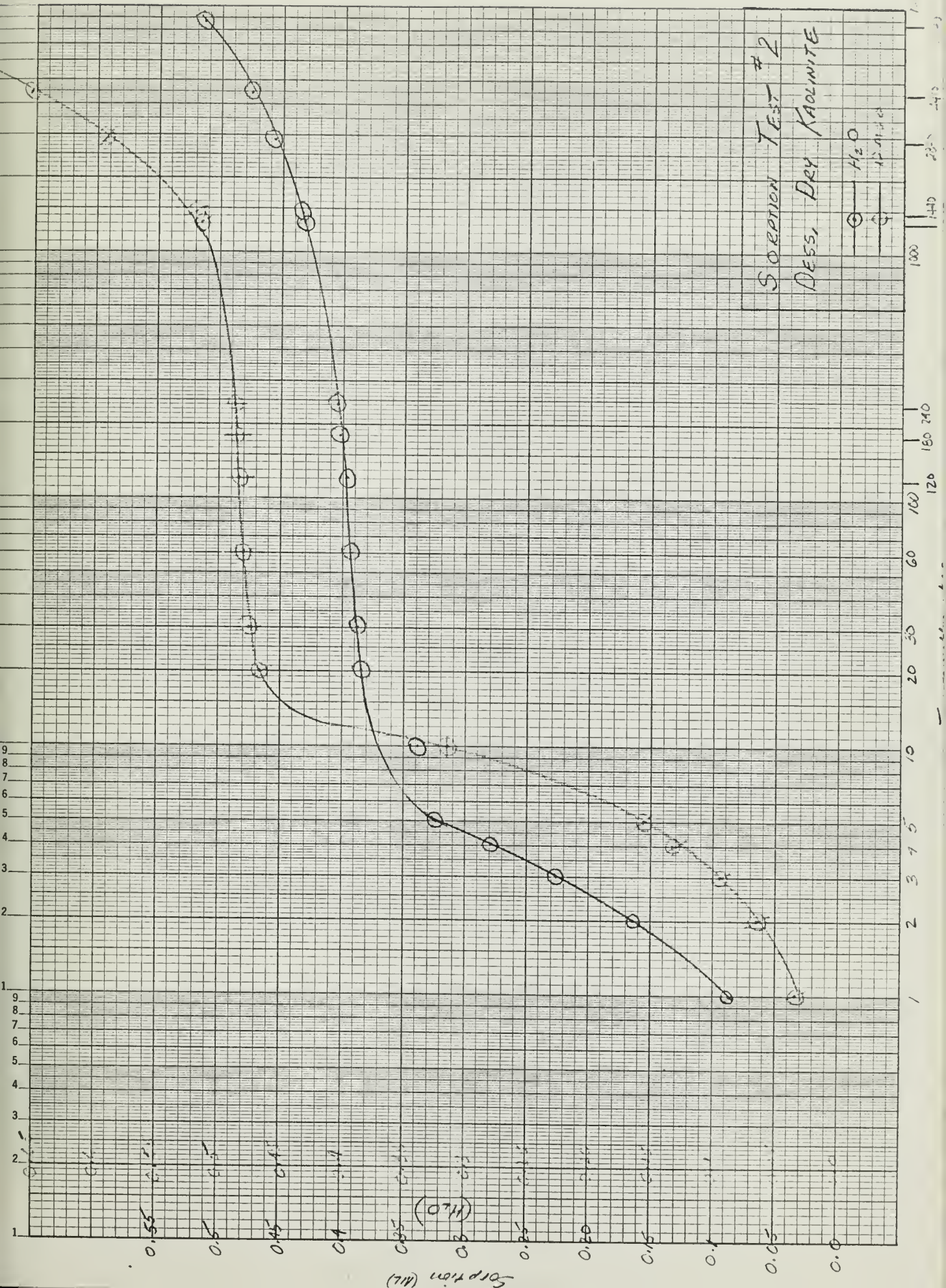
Original Moisture Contents

0.05%

7.4%

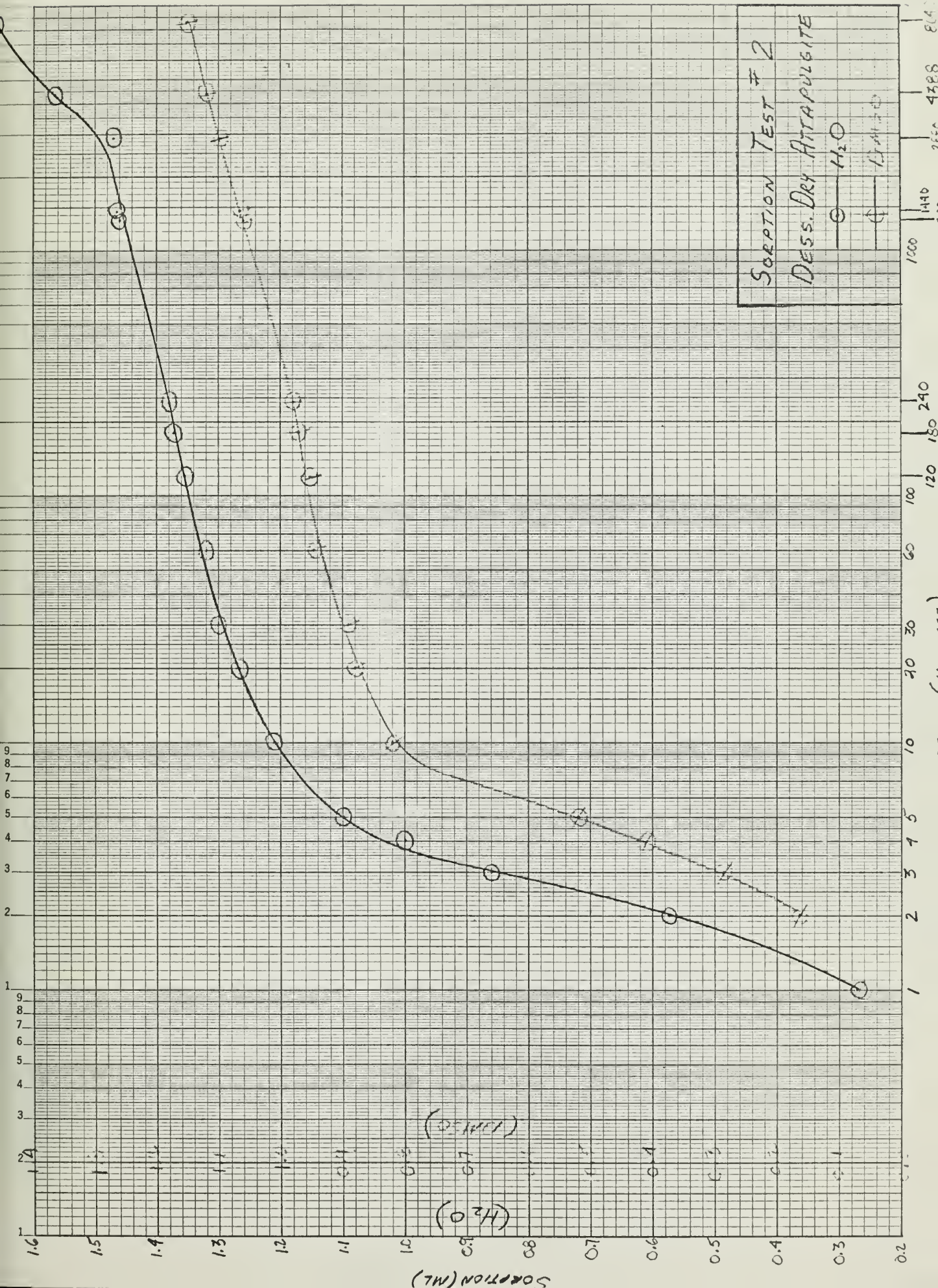
4.9%





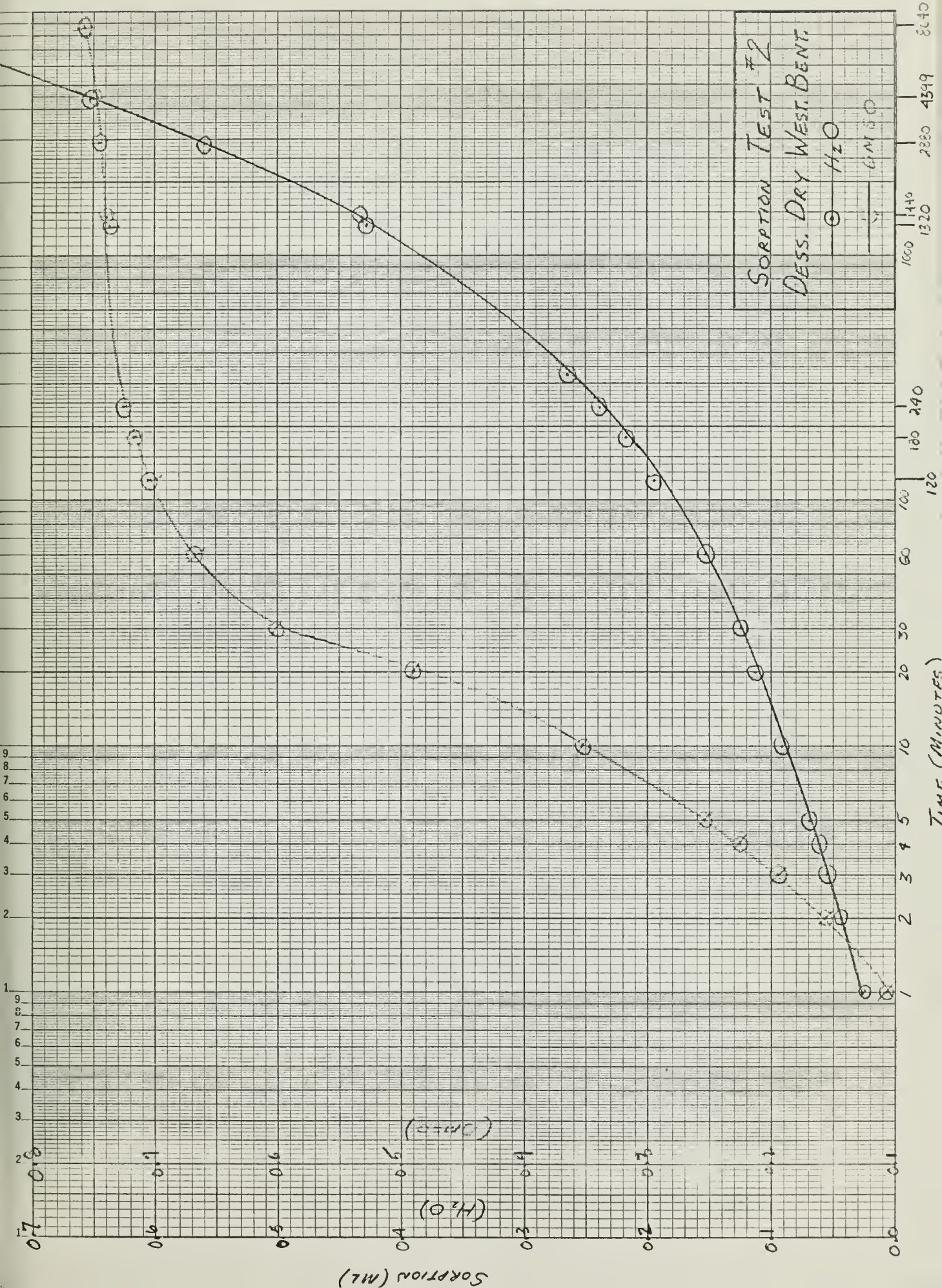
















### E. Sedimentation Volume

The sedimentation volume test is one which measures the flocculated solid volume of a clay liquid suspension after a certain period of time. The test was first developed by Hoffman around 1945 in Germany, and was used mainly to find the effect of different cations and different particle sizes on the flocculated volume of a bentonite soil [6].

It is a well known phenomenon that in hydrated clay soils, polar liquids are affected by both the strong force fields which emanate from the particle and the cations that are associated with this force field. This process which results in ion solvation and bonding of the polar liquid to electrically charged surfaces also causes a certain restriction on the movement of the liquid molecules resulting in the loss of some of their kinetic energy which is given off as heat (heat of wetting) in the dispersion of solid particles. Besides this effect these cations which are held by the force field of the clay particle would also like to dissociate in the solvent media. An analogy can now be drawn between this situation and a solution in a semi-permeable bag placed in some vessel containing pure solvent. If this semi-permeable bag allows solvent to pass through but not the solute then a pressure gradient will be created at the semi-permeable membrane. This same type of pressure gradient is formed in a clay dispersion because certain of the cations are bound by the force field of the clay particle. This results in the formation of an artificial membrane around the clay particle. The solute that is attracted around the clay particle due to this tendency of the solvent ions to disperse has become known as



osmotic water and the resultant action has become known as the osmotic swelling in clay soils [22]. Further "the structural unit of a particle with its surrounding cation swarm is called a micelle" [24].

This osmotic swelling and formation of micelles is very important in the sedimentation volume test. The amount of osmotic swelling or the size of the micelle are important factors in determining how dense a flocculation of particles may be. For example, if one has large swelling with a resulting large micelle then one would expect that the soil particles themselves in a flocculation would be further apart therefore giving a larger sedimentation volume than if there was less swelling around the particle. For this reason these very simple sedimentation volume tests for different polar liquids may give some idea of the various osmotic reactions which are one of the most important aspects of the soil-liquid interaction.

The sedimentation volume test done in this study was patterned after the method used by Hoffmann. The test consisted of placing a small weighed amount of oven dry soil in a graduated stoppered glass cylinder (Fig. 14). Next a measured volume of liquid was placed in the cylinder and the cylinder was shaken by hand for approximately two minutes to thoroughly disperse the soil in the liquid. Then the cylinders were allowed to stand for twenty four hours in a constant temperature bath. It was found that this length of time was sufficient to allow most of the soil particles to settle into a flocculated volume at the bottom. Then the sediment volume was read to the nearest  $\pm 0.5$  ml. The test was also run varying the temperature in the bath from approximately 23.5°C (room temperature) to about 50.0°C.





FIGURE 14  
STOPPERED GLASS CYLINDERS  
USED IN  
THE SEDIMENTATION VOLUME TEST



In one instance the sample cylinders were placed in a refrigerator at a temperature of  $6.0^{\circ}\text{C}$ , but it was only possible to read the volume in the water test since the DMSO freezes at this temperature.

The volumes were measured using 10 gm. of oven dry Kaolinite, 5 gm. oven dry Attapulgit, 5 gm. of oven dry Western Bentonite and 50 ml., 50 ml. and 75 ml. respectively of the three liquids.

The results of the test at various temperatures are given in Table 8 while the sedimentation volume per gm. of soil is given in Table 9. Also a modified void ratio has been calculated and tabulated in Table 10.





TABLE 8

	Temper- ature	Kaolinite		Attapulgate		West.Bent		Soil Type
		Solid	Liq.	Solid	Liq.	Solid	Liq.	Sediment Vol.& Liq.Wt.
	↓	With Water as the Liquid						↓
Run #1	23.5°C	30	53	47	51	77.5	77.5	
	32.0°C	30	53	47	51	77.0	77.0	W
	42.5°C	32	52	49	50	77.0	77.0	A
	50.8°C	33	52	47.5	47.5	78.	78.0	T
	6°C	28.8	50	50	51	77	77	E
Run #2	22.2°C	30	51.5	50	51	77	77	
	30°C	30	51.0	50	51	77	77	R
	40°C	31	51.5	50	51	77	77	
	50°C	33.5	51.5	50	51	78	78	
Run #3	22.4°C	30	50	49	50	77.5	77.5	
Run #1	23.5°C	43	52	19.5	52	13	77	
	32.0°C	43	52	20	52	13	77	
	42.5°C	43	52	19.5	52	13	78	D
	50.8°C	43	52	20.5	53	13	79	
	6°C	← F R O Z E N →						M
Run #2	22.2°C	42.0	50.5	20.5	51	13	76	S
	30°C	42.0	50.5	20.5	50.5	13	77.5	
	40°C	41.5	51	20.5	52	13	78	O
	50°C	43	50.5	22.5	52	13.0	79	
Run #3	22.4°C	28.5	53.2	13.7	52	14.0	76.5	DMF



TABLE 9

Avg. Sediment Volumes at Room  
Temperature  $\sim 22.7^{\circ}\text{C}$  per gram  
of soil<sup>#</sup>

Soil			
Liquid	Kaolinite	Attapulгите	Western Bent.
Water	3.0	9.74	15.45 <sup>*</sup>
DMSO	4.25	4.0	2.6
DMF	2.85	2.74	2.8

<sup>#</sup> Assuming gel volume varies directly with the soil wt.

<sup>\*</sup> Gel filled entire volume.



TABLE 10

Modified Void Ratio for Sediment Volume

$$e_m = \frac{\text{Volume of clear liquid}}{\text{Volume of Sediment}}$$

	Temperature	Kaolinite (10 gm.)	Attapulгите (5 gm.)	Western Bent. (5 gm.)	
Run #1	23.5°C	.767	.0851	0	
	32.0°C	.767	.0851	0	
	42.5°C	.625	.0204	0	W
	50.8°C	.576	0	0	A
Run #2	6°C	.736	.020	0	
	22.2°C	.716	.020	0	T
	30°C	.700	.020	0	E
	40°C	.661	.020	0	
	50°C	.537	.020	0	R
Run #3	22.4°C	.667	.0204	0	
Run #1	23.5°C	.209	1.667	4.923	
	32.0°C	.209	1.600	4.923	
	42.5°C	.209	1.667	5.000	
	50.8°C	.209	1.585	5.077	D
	6°C	← F r o z e n →			M
Run #2	22.2°C	.202	1.488	4.846	
	30°C	.202	1.463	4.962	
	40°C	.229	1.536	5.000	S
	50°C	.174	1.311	5.077	O
Run #3	22.4°C	.867	2.796	4.464	DMF





F. Investigation of Secondary Aggregation

The formation of secondary aggregations or macroscopic soil structure as per Winterkorn is a phenomenon associated with water loss and the resultant shrinkage of swelling cohesive soils. The forces that cause these formations are usually related to cultivation of the soil, the root activity of plants and the freezing and thawing and wetting or drying of the soil by meteorologic cycles. As the water is lost from the cohesive soil, shrinkage occurs with resulting tension forces being formed in the drying surface layer. The stresses that are built up are relieved initially by plastic flow in the material. However as the soil becomes drier it loses its plastic properties and the stresses can be relieved only by cracking of the soil. This cracking generally proceeds according to the law of least energy, giving the greatest stress relief for the smallest work. The precise law which the soil follows is a special case of the law of least energy known as the triple angle law. This triple angle law predicts the formation of cracks in three directions from a point, with an approximate equal angle of  $120^\circ$  between the cracks. As a large number of cracks begin to form in the soil they usually run together to form polygons, the most common of which is the hexagon [22]. Actually the law predicts the formation quite accurately as can be seen by the photographs taken of the soils tested in this report.

The actual occurrence and size of the shrinkage phenomenon depends on a number of factors including soil type, drainage surfaces, thickness of dried layer, homogeneity of soil and type of liquid in the soil. This test is important in that it is a



good indicator of the potential of different soils and various liquids to form secondary aggregations. These secondary aggregations are important, in that they form the basis for the stabilization of the soil. Stabilization is produced through the secondary aggregations not the primary soil particles. Further these formations give a deeper insight into the soil-liquid interaction.

The test to determine the secondary aggregation was carried out as follows:

1. Oven dry samples of the three soil types were mixed above the liquid limit with the three liquids.
2. The mixtures were allowed to stand in dessicators overnight so the liquid might reach equilibrium with the soil.
3. Next the soil was spread in a thin film on a unglazed porcelain plate, and allowed to dry. The shrinkage cracks could then be photographed.

There are a few important considerations in running this test. First an unglazed porcelain plate was used since it permitted drainage from the underside of the sample besides evaporation from the surface. Secondly, it was important to insure that the films of the same soil with the different liquids were of approximately of the same thickness. This was accomplished by placing two parallel layers of masking tape on the porcelain plate. Then the sample was placed between these strips of tape and spread by sliding a spatula on the tape and over the sample. This resulted in the thickness of the sample being approximately the same as the thickness of the layers of tape used in the respective test. One layer of tape was about 0.15 mm. thick.



The results of these tests are illustrated by Figures 15 - 24. The strips of Attapulgite shown are approximately 0.15 mm. thick while the strips of Kaolinite and Western Bentonite are approximately 0.45 mm. thick.





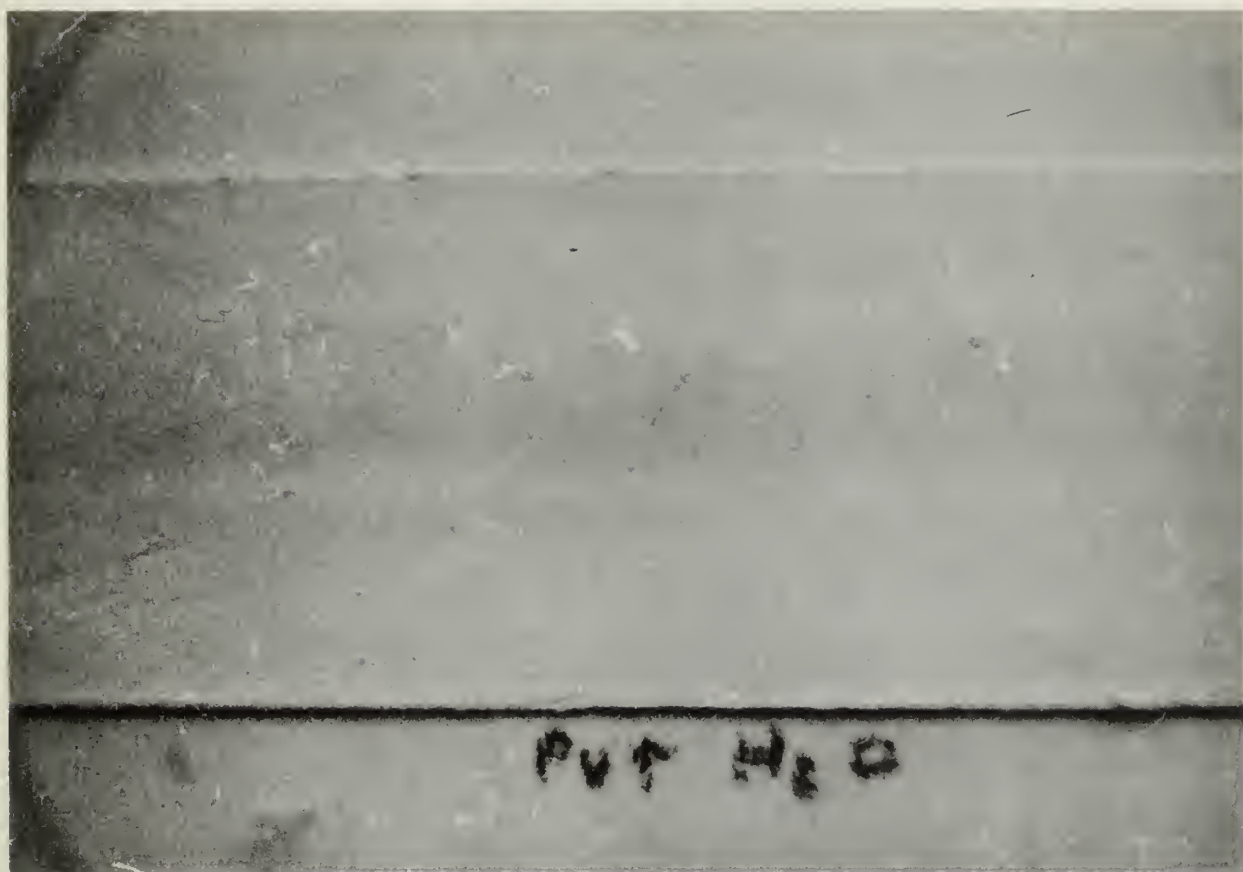


FIGURE 15  
KAOLINITE - WATER





FIGURE 16  
KAOLINITE - DMSO



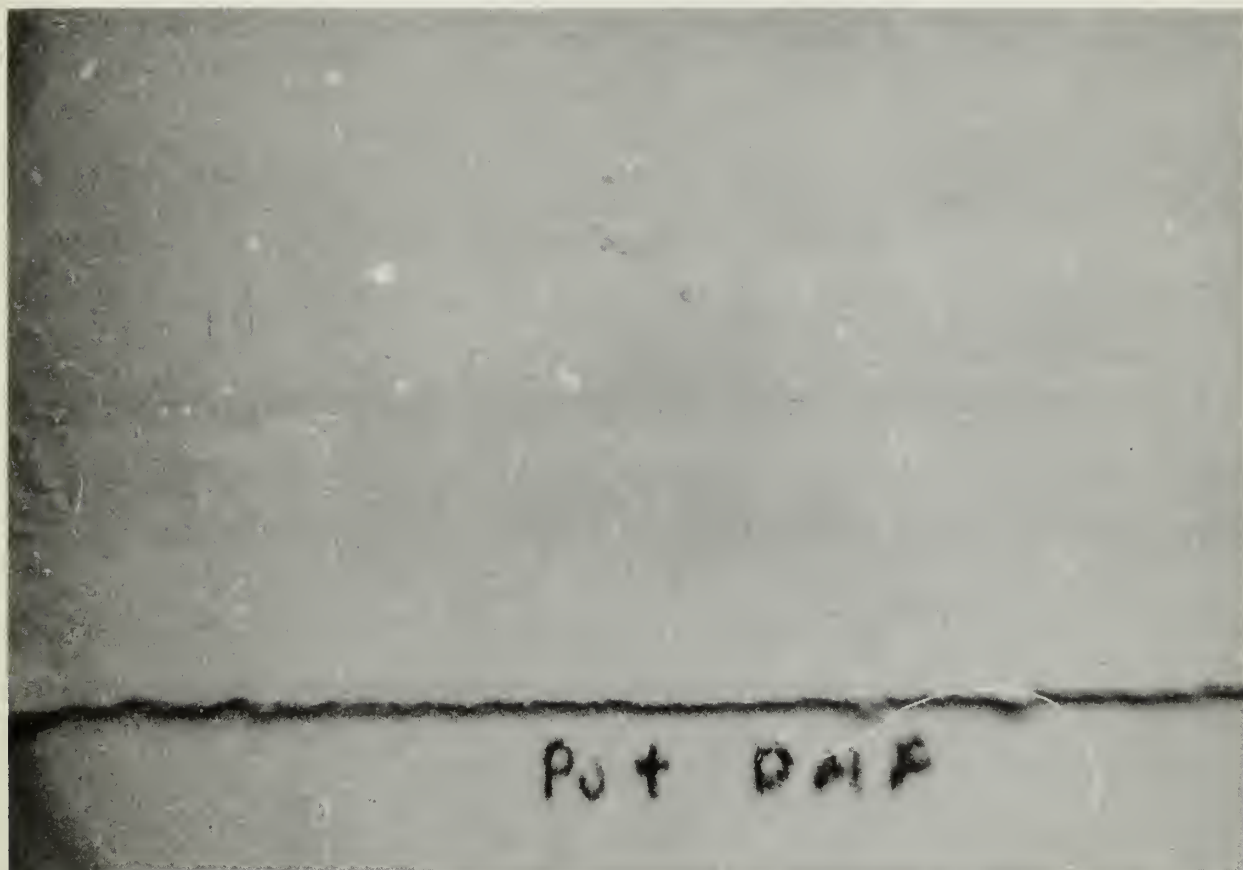


FIGURE 17  
KAOLINITE - DMF





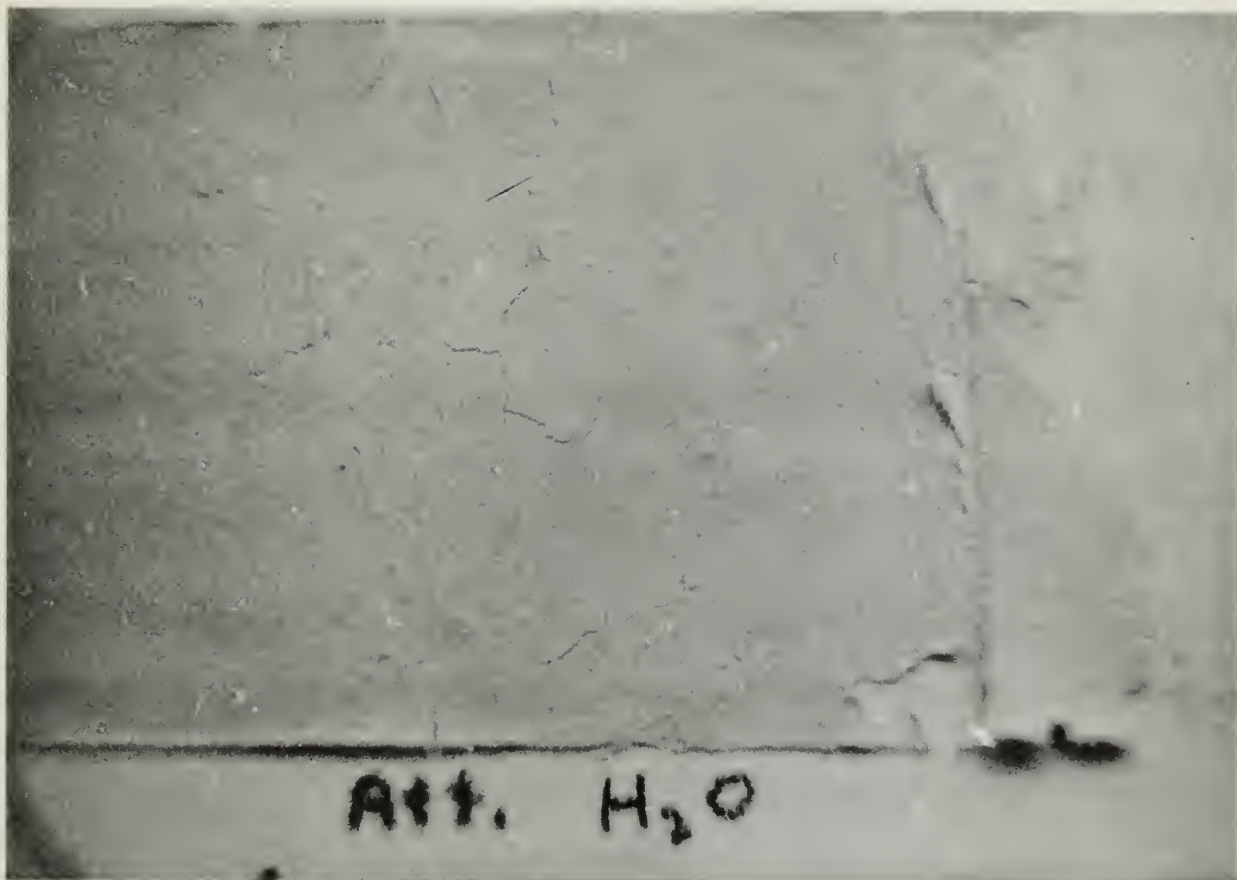


FIGURE 18  
ATTAPULGITE - WATER



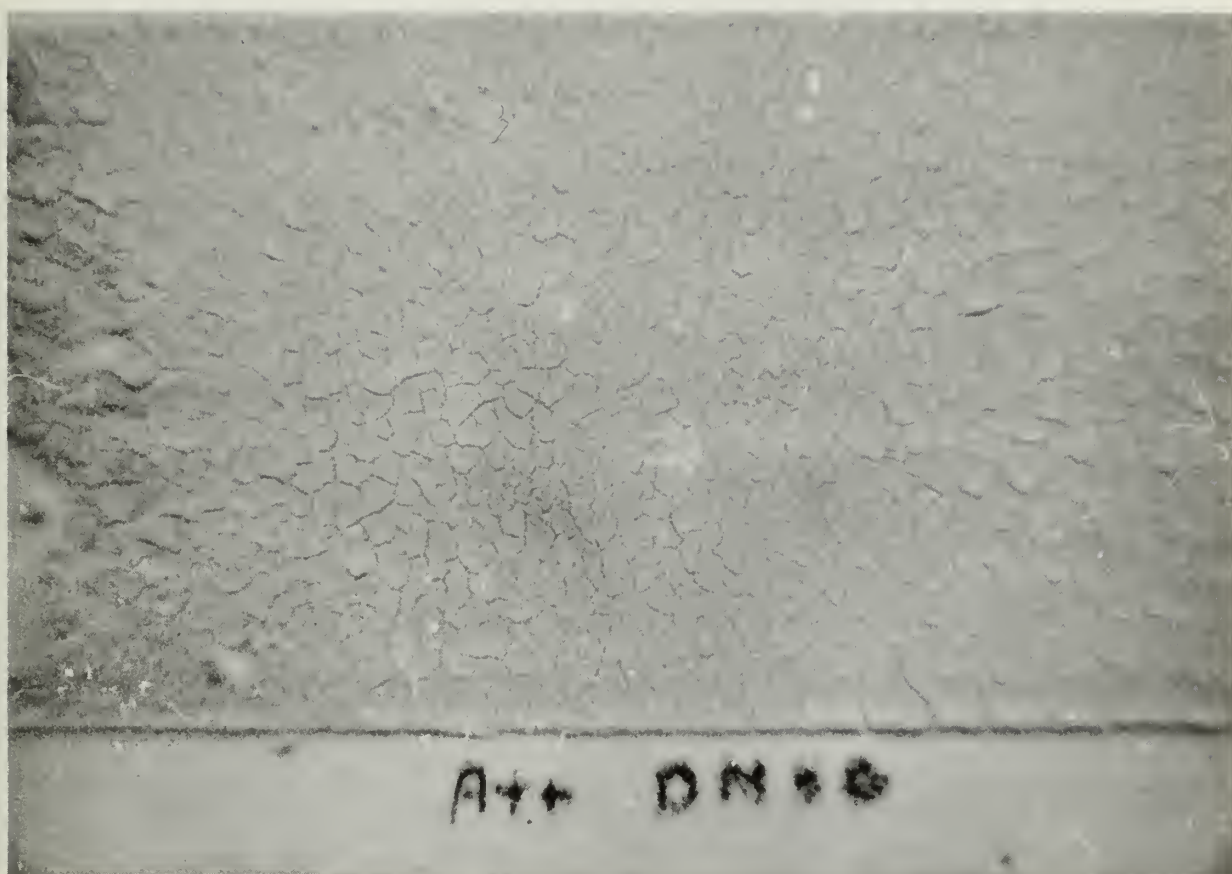


FIGURE 19  
ATTAPULGITE - DMSO



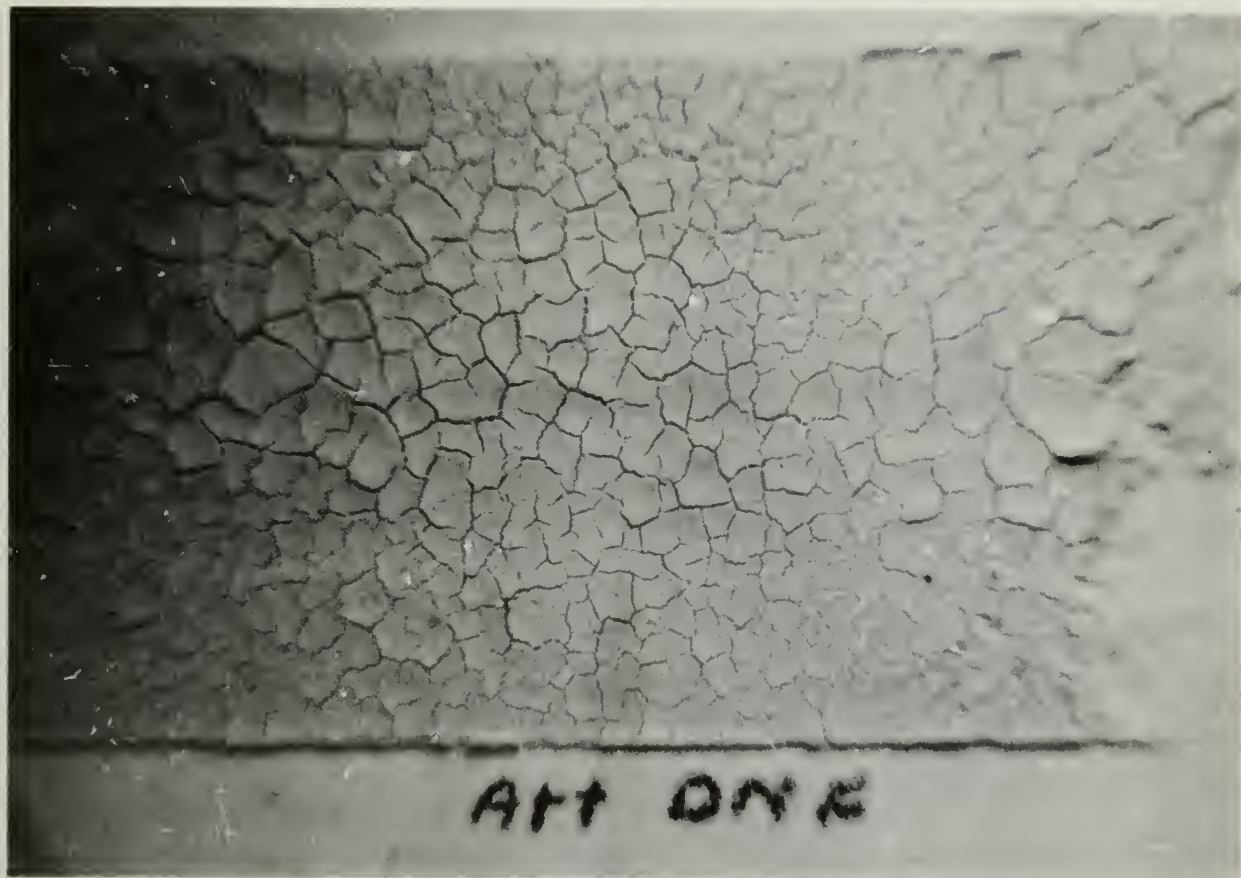


FIGURE 20  
ATTAPULGITE - DMF





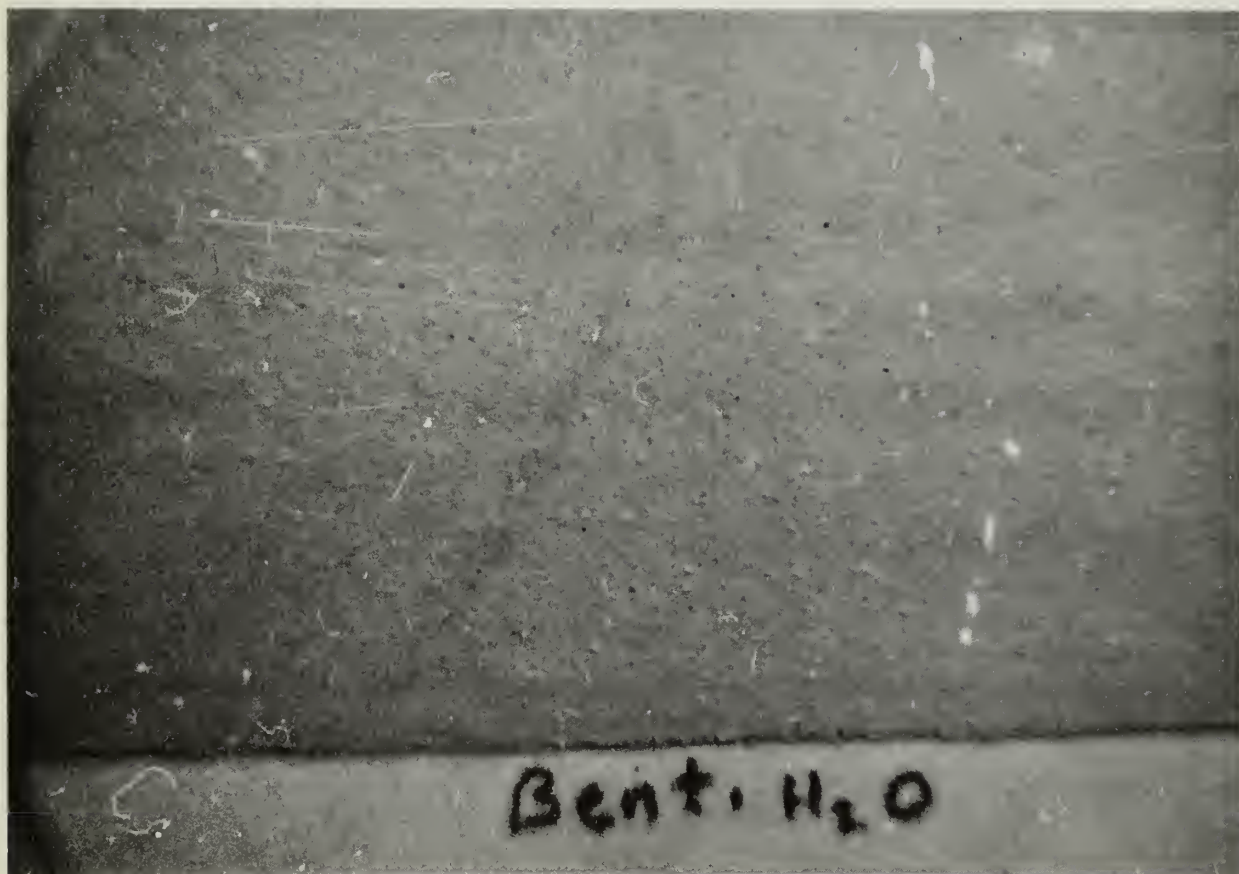


FIGURE 21  
WESTERN BENTONITE - WATER





FIGURE 22  
WESTERN BENTONITE - DMSO







FIGURE 23  
WESTERN BENTONITE - DMF





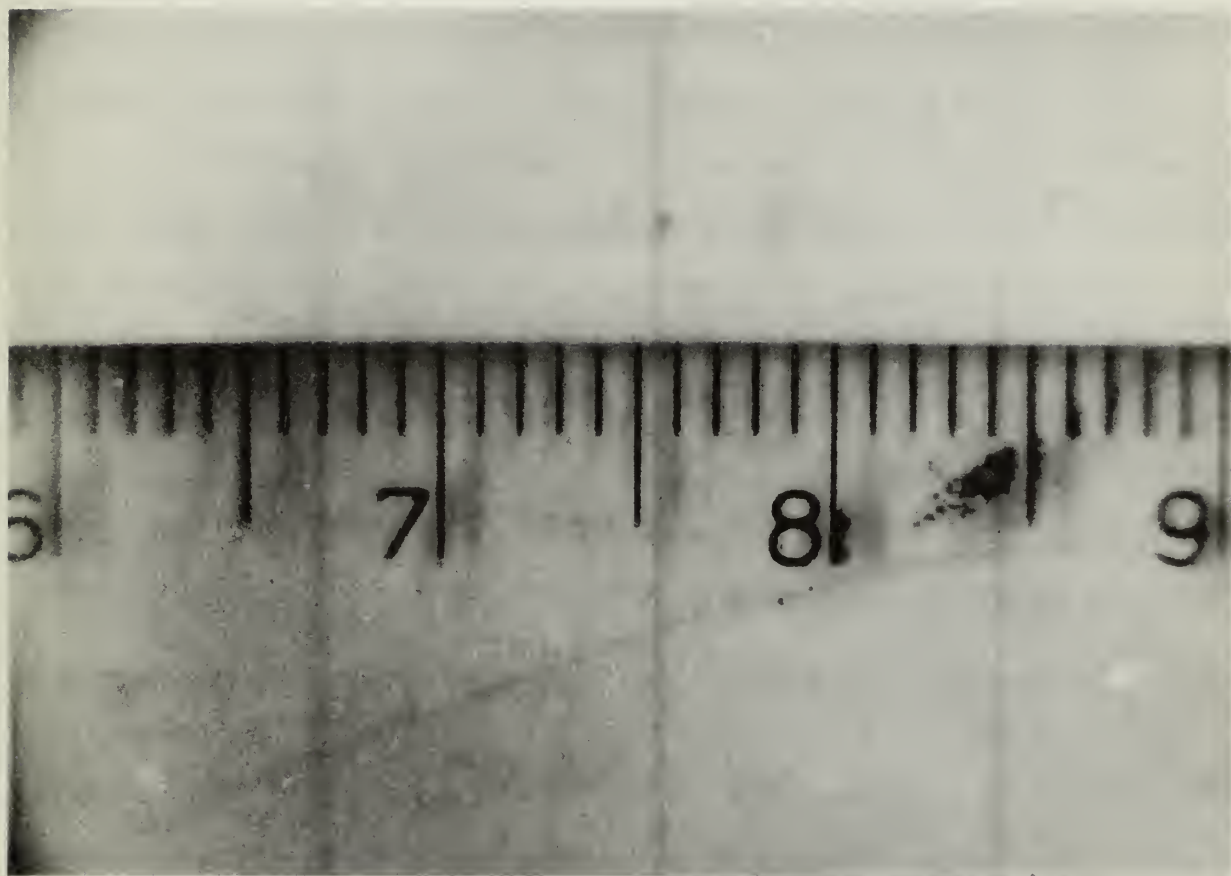


FIGURE 24  
SCALE IN mm.



### III. DISCUSSION OF EXPERIMENTAL RESULTS

#### A. Atterberg Limits

The results of the Atterberg Limit Tests (liquid limit, plastic limit, and plasticity index) are indicated in Table 3. The plasticity index is a representation of the moisture range in which plastic properties dominate the soil behavior. It is somewhat analogous to the melting point - Boiling Point range. Water, for instance, has a much greater melting point - Boiling point range than similar materials in the Periodic table such as  $H_2S$  or  $H_2Se$ , due to the fact that it has a strong, directed, intermolecular-bonded structure. In the same manner, the larger plasticity index is indicative of a greater liquid-soil particle surface interaction or stronger cohesive forces between the soil particles.

The importance of the plasticity index for soils is shown by the fact that the American Association of State Highway Officials uses as criteria for their (AASHTO) Classification of Highway Subgrade Materials the mechanical analysis of the fraction retained on the number 200 sieve and the liquid limit and plasticity index of the fraction passing the number 40 sieve [22].

The Atterberg Limits are indicators of the water affinity, clay mineral content and susceptibility to volume changes of the material being tested. However, they do not represent simple physical properties but rather are a composite result of several soil properties including particle shape, specific surface, elasticity, porosity, water affinity and interparticle attraction and repulsion of the solids.



In the tests with water, it appears that the plasticity index varies proportionately with the base exchange capacity of the clay. This would appear consistent with the water affinity and swelling of the clays increasing from Kaolinite through Attapulgite to Bentonite. In DMSO, no such trend is evident. Comparing the plasticity index of Bentonite with water and DMSO, the index is significantly less in DMSO. This would indicate less interaction of Bentonite with DMSO than with water. This may be caused by the fact that DMSO, due to its molecular structure and diffuse positive dipole charge does not solvate anions and thus does not interact with the surface of the Bentonite to the extent that water does with its hydrogen bonds. It logically follows that there would be little or no "ice" (less dense) DMSO layer around the Bentonite and this is borne out in the specific gravity tests, which will be discussed in the next section.

The plasticity index variation of the Kaolinite is directly opposite to the variation shown by the Bentonite. Kaolinite's plasticity index is increased significantly (almost doubled) with DMSO than with water. This would indicate a greater interaction with DMSO and would tend to corroborate observations which indicate that the Kaolinites normally have a greater affinity for certain organic liquids than for water. This phenomena is little understood but may be related to the molecular size and structure of the organic liquids. Waidelich [20] in his investigations in 1957 tested for the plasticity index of Kaolinite with various organic liquids. His data indicated the plasticity index as compared with that with water was less for methyl and ethyl alcohol and larger for propyl and butyl alcohol. The molecular weight and size increases with these alcohols, which could infer that





the molecular size and structure may have a bearing on the Kaolinite-organic liquid phenomena and which may warrant further investigation.

The plasticity index of Attapulgite varies only slightly with water and DMSO, being a little less with the organic liquid. This would indicate a slightly decreased interaction with DMSO than with water.

In essence, the Atterberg limit tests indicate a greater soil - DMSO interaction for Kaolinite and a greater soil-water interaction for Attapulgite and particularly for Bentonite.

#### B. Specific Gravity

As stated in the description of experiments it has been shown particularly by E. W. Russell [17] that the specific gravity of a soil material is not only dependent on the type of soil but also upon the properties of the liquid used in the test. Specifically for polar liquids it appears that both the geometry of the molecules and the electric properties of the liquid are important factors in the soil liquid interaction. Further it seems that these electrical and geometrical properties could have profound effects on the specific gravity determination.

The specific gravity of a soil material is obtained using the method in section III from the following formula [1].

$$\text{Sp. Gr.}(T_x) = \frac{W_s}{W_s + W_{L(T_x)} - W_{Lsm}(T_x)}$$

Sp.Gr.( $T_x$ ) = Specific gravity at a temp.  $T_x$

$W_s$  = Weight of a quantity of over dried soil (gms.)

$W_{L(T_x)}$  = Weight of a small bottle filled with water at a temp.  $T_x$  (gms.)



$W_{Lsm}(T_x)$  = Weight of the same small bottle filled with a liquid soil mixture at temp.  $T_x$  (gms.)

It is obvious that the bottom portion of this equation represents the weight of the liquid displaced by the soil particles which in the case of water also gives the apparent volume of the soil particles. In the case of liquid with specific gravities different from water the weight of the liquid displaced must be divided by its respective specific gravity to give an apparent volume or equivalent weight of water displaced. For a respective soil sample, if the soil-liquid interaction was the same for all the liquids, one would obviously expect to calculate the same specific gravity for the sample in different liquids. However if there are different interactions with different liquids then one would expect to obtain different specific gravities for our sample. Assuming the weight of the soil to be equal in all tests this would further mean that our apparent soil volume or equivalent weight of water must vary. For example comparing two liquids, if it was found the specific gravity in liquid A was higher than in liquid B, it might infer that the apparent volume of soil or equivalent weight of water displaced in liquid A was less than in liquid B, meaning also that the combined equivalent weight of water and soil in liquid A is larger than in liquid B. This then would also mean that it appears that the equivalent water has a denser configuration around the soil particle in liquid A than in liquid B.

Considering now the character of water closely associated with the surface of the soil, we can actually describe several states. From Winterkorn [22] these states are: a) the solid



solution in the surface layer of the mineral particles; b) the oriented condition on the surface resulting from the superposition of geometrical wall effects and the negative electrical character of the mineral surface. In the case of montmorillonite, ~~lawe~~ has shown this layer to be less dense than water and similar to normal ice; c) cation hydratation due to the effect of a strong point charge in the polar liquid. The water may be denser around the cation than ordinary water; and d) relatively free water with a structure similar to normal water but influenced by the osmotic effect. Polar liquids other than water will also have these structures influenced in some manner by the characteristics of the mineral. The effects that cause these various structures concern the geometrical and electrical properties of the clay mineral plus the dipole moment, the dielectric constant and the geometrical structure of the polar liquid.

Now that some of the possible interactions and their effect on the specific gravity have been discussed it is important to relate these phenomena to the results of the specific gravity tests found in the experimental portion of this report.

For Bentonite it appeared (Table 4) that the mineral had a higher specific gravity in DMSO than in water. From previous discussion it might be inferred from this that the apparent density of the liquid around the Bentonite particles in water was less. Actually it appears that this may be true since the water structure around the negative-charged surface of the Bentonite mineral and that between the expanding lattices has been described as similar to ice or less dense than water. With the DMSO liquid there is no apparent similar effect because the





DMSO molecule cannot form strong hydrogen bonds with the negative surface of the mineral. Since this ice-like structure can be quite substantial in the case of Bentonite it would seem that this may be the important factor affecting the specific gravity. Also important of course would be the effect of the dielectric constant, dipole moment and the geometry and size of the molecule but these effects are more difficult to describe.

In the cases of Attapulgite and Kaolinite it was found that larger specific gravities occurred with water, the opposite of the Bentonite case. This is logical for the previously discussed ice effect which occurred in Bentonite does not appear to occur in Attapulgite and Kaolinite. It seems as already mentioned that the larger specific gravity in water would indicate a greater apparent density of liquid around the particle. For Kaolinite this might be explained by the non uniform negative electric surface of the mineral. Other investigators have found that in Kaolinite a contraction effect may occur on the surface of the mineral resulting in a denser water structure than normal. As for Attapulgite it appears that the geometric size and shape of the molecules may become important. DMSO is a larger molecule than the water and also since it has little affinity for anion type surfaces it may not fit or will not be drawn as strongly as the smaller water molecule into the tubular center of the clay particle. This conclusion could possibly be further verified by observing that substantially more water than DMSO was sorbed into the Attapulgite sample in the sorption test. The above consideration may well explain the fact that larger specific gravities



occurred with these two minerals in water. Again other characteristics of the liquids and minerals are important but are more difficult to describe.

### C. Dietert Compaction Test

The results of the Dietert Compaction Tests for optimum liquid content are indicated in Table 5 and are based on the data graphically represented. The optimum moisture content is found in the graphs by finding the liquid content at the minimum sample length.

The increase in the optimum liquid content of the Kaolinite with DMSO over the Kaolinite and water can be attributed to the greater affinity for DMSO rather than water. This is consistent with the other test results for Kaolinite.

For Attapulgite, there is a smaller affinity for the DMSO than for water as indicated by the decrease in the optimum liquid content for the Dietert tests with DMSO than with water. This may be attributed to the structure of the liquids and the effect of the dielectric constant of the liquids. The water molecule is smaller than the DMSO molecule and this may prevent or diminish the intake of the DMSO molecule into the channels in the Attapulgite. Additionally, the greater dielectric constant of the water over the DMSO allows greater osmotic swelling and a large micelle size in the water.

At first glance considering the results of the test of Bentonite with the liquids it might appear that the optimum liquid content would be less than 10%, because the maximum density occurs near this point. However maximum density is not the only



consideration for optimum liquid content. Also included in this concept particularly for very active soils, is the satisfaction of the major part of the water affinity of the soils. The Plastic Limit is a good indication of this satisfaction and for this reason gives a more realistic value for optimum liquid content. The values given in Table 5 are approximately at the Plastic Limit of the samples. Further it is important to remember that the optimum liquid content is dependent on two physical-chemical phenomena, liquid affinity and lubrication. The liquid added to the system is initially required to satisfy the liquid affinity. Only after this affinity has been satisfied can additional liquid be used for lubrication in the system, thereby allowing a decrease in density. In the case of Bentonite and Water this affinity and the resultant osmotic swelling are so great that lubrication can never become substantial enough to allow densification. These factors result in a consistent decrease in density from the moisture content of 10% up. However in the case of Bentonite and DMSO it was observed (see plot of sample length vs. liquid content of Bentonite and DMSO) that at approximately the plastic limit enough lubrication occurred to allow a slight increase in the density of the sample. These indicators seem to be consistent with other tests concerning Western Bentonite and the liquids.

#### D. Liquid Sorption Test

The results of the liquid sorption test indicate a greater intake of water for the cases of Bentonite and Attapulgite and a greater intake of DMSO liquid for the Kaolinite clay. The results of this test are represented in Tables 6 and 7 and seem to





correlate quite well with the data obtained from other experimental work in this report and the data obtained by Winterkorn and Bayer [23]. The results of this test are expressed as total sorption of liquid per 0.5 gm. of soil sample. Although Bayer and Winterkorn split up the total sorption in their tests into swelling water and pore water, it was felt it was not necessary to do this in this work. Since the void ratios were approximately the same for the same soil types, this meant that the pore water would also be equal for the same type of mineral. Therefore a comparison of total sorption values, although not an indication of the quantity of swelling liquid, certainly gives a qualitative indication for comparison of the osmotic or swelling values for the two liquids.

Considering Bentonite first it is seen that over a long period of time the sorption is much greater with the water. The sorption of water seems to proceed quite slowly at first because of the tremendous swelling of the clay particles. This large swelling seems to have the effect of reducing the effective pore size and thereby reducing the amount of capillary flow into the upper portions of the sample. With the smaller swelling with the DMSO liquid, this effective pore size is not reduced so drastically and the sorption can proceed much more rapidly. These conclusions are borne out by the data which illustrates the sorption of the DMSO proceeding much more rapidly up to approximately 4400 minutes. The results of this work also bear out the conclusion that Bayer and Winterkorn reached concerning the decrease in swelling with a decreasing dielectric constant for the expanding lattice clays. DMSO has a dielectric constant of about 49 while water has one of approximately 80. This result can be further



verified by considering the equation for the force between two electric charges. The force is represented by

$$F = \frac{e_1 e_2}{Dr^2} .$$

If the dielectric constant is multiplied by approximately two, this means for the same radius and charges, the force between the particles in water would be approximately one half of what it is in DMSO. This allows the dispersive kinetic energy of the particle (cation) to prevail more in water allowing the positive ion to move a greater distance from the mineral surface. This results in an increase in dispersion of cations and a greater liquid intake causing the larger osmotic swelling and micelle size in water.

For the case of Attapulgite it is also observed that there is a greater swelling in the water. This increased swelling is probably caused in part by the same phenomena that caused the larger swelling of Bentonite with water, the dielectric constant effect. However there is one important basic difference in the swelling of the two soils which seems to indicate that other factors are involved. In the case of Attapulgite the sorption of water was always larger for any given time than the sorption of DMSO, while for Bentonite initially the sorption of DMSO was larger. This perhaps may be explained by considering the configuration of the Attapulgite mineral and the different geometric sizes and electric characteristics of the liquid. One of the main reasons for the large water affinity of the Attapulgite mineral besides its fairly high BEC is its structure, or the fact that it has a channel between its layers (Fig. 5). This channel



has negative surfaces surrounding it and is large enough to allow a double layer of water molecule to enter. Since the DMSO molecule is substantially larger than the water molecule ( $\Gamma_{H_2O} \approx 1.38$ ,  $\Gamma_{DMSO} \approx 2$  or  $3.1$ ) and has less affinity for negative particles, it may not move into this channel as easily as the water. This might account for the fact that the sorption of water at any instant is larger than the sorption of DMSO. Another consideration however is the fact that in Attapulgitte and water the swelling does not seem to be as large as in Bentonite and water, so the effect of reduction in effective pore size is not critical.

Finally it was observed that the sorption of DMSO was larger than water in the Kaolinite soil. This would seem to indicate that perhaps the swelling was greater for Kaolinite and DMSO than for Kaolinite and water. However considering the dielectric constants this does not seem possible so another theory must be postulated. It seems that perhaps a greater hydration of the cations by DMSO might cause this occurrence but it is difficult to predict. Still as stated in the section concerning the Atterberg limits it has been observed by others that Kaolinite has a tendency to sorb more of certain organic liquids than water. No firm explanation has yet been given for this phenomenon.

#### E. Sedimentation Volume

The results of the sedimentation volume test are indicated in Table 8, a modified void ratio is shown in Table 10, and the average sediment volumes per gram of soil are shown in Table 9.

As mentioned in the previous discussion of the sedimentation volume test, the test should be a measure of the liquid affinity





of the clay minerals, specifically in their ability for osmotic swelling, micelle formation and flocculation. In order to allow a better comparison between each mineral and the liquid used, the modified void ratio concept was used. The modified voids ratio is actually the volume of clear liquid to the volume of sediment. Thus, the larger the value of the modified voids ratio, the lesser the value of the sedimentation volume. A value of zero for the modified voids ratio would indicate a complete or thixotropic dispersion. Obviously, the higher the modified voids ratio, the lower the liquid-soil interaction.

Due to the fact that different weights of the three clays and different volumes of the liquids were used, a direct comparison between the different clays and liquids using the modified voids ratio is not feasible. The basic reason for utilizing different volumes of liquids and different weights of the clays was the marked variance of the liquid interaction with the clays.

However, using the average sediment volumes per gram of soil, one can infer certain comparisons between the different clays and liquids. Thus, in the tests with water, the Bentonite was most active, the Kaolinite least active, and the Attapulgite somewhere in between. Actually, the Bentonite was thixotropic in the water. These results are consistent with other test results. In the tests with DMSO, the Kaolinite had the most interaction, the Bentonite the least and the Attapulgite was in intermediate position. This again is consistent with previous results for the reasons previously explained. In the tests with the DMF, there is no great difference in the sediment volume per gram of



soil, indicating all clays had essentially the same degree of interaction.

Bentonite as shown from the modified voids ratio data and the sediment volume per gram of soil is significantly more active in the water than in either the DMF or DMSO. It has a slightly lesser interaction in DMSO than in DMF but the variance from the data is slight and is not sufficient to be significant. The greater activity of Bentonite in water can be attributed to the greater micelle size and the greater dielectric constant of the water than either DMSO and DMF. For the Attapulgate, the results were approximately the same as with the Bentonite, that is, the Attapulgate had greater interaction with water than with DMF and DMSO. The Attapulgate was slightly more active in the DMSO than in DMF. The reasons for this are as previously described.

In the Kaolinite, the data indicate greater activity in DMSO, least activity in DMF, with Kaolinite-water interaction approximately the same as the Kaolinite-DMF. The Kaolinite has greater affinity for certain organic liquids and thus might have a greater interaction with DMSO than water. Also, the flocculation phenomenon enters into the sedimentation volume test. Kaolinite has "broken bonds" on the edges and this results in positive and negative charges on the edges. The flocculation phenomenon is greater in the DMSO than in water because the DMSO does not solvate anions while the water solvates or shields both anions and cations. Thus flocculation can occur to a greater degree in DMSO than water. The Kaolinite-DMF interaction, however, produced rather strange results. Since DMF, like DMSO, is an organic, polar liquid with the property of not solvating anions,



one would expect to find the same results as compared to water as the DMSO. This was not the case. Instead, the results indicate that the Kaolinite and DMF have slightly lesser interaction than Kaolinite and water. This appears inexplicable. For reasons expressed previously, the full series of tests were not conducted with the DMF, and consequently, the results of the other tests are not available for comparison. It would appear that the DMF-clay interaction would be worthy of further research to perhaps shed new light on the Kaolinite-organic liquid interaction.

The test runs in the temperature bath indicated no change in the activity of the Bentonite and water, that is, it remained a thixotropic dispersion. For the Kaolinite and water, the increase in sedimentation volume with increased temperature could be attributed to a flocculated structure. The increase in temperature would cause greater flocculation, thereby giving increased sedimentation volume.

In the DMSO and Bentonite, as the temperature increased, the sediment volume decreased, indicating a decreased interaction. This may be attributed to the fact that as temperature increases, the dielectric constant decreases and the kinetic energy of the cations increases. This would tend to increase the electric force field and shrink the micelle, thereby decreasing the interaction of the clay and DMSO. The Attapulgit and DMSO showed an interesting variation as the temperature increased. The modified voids ratio first decreased then increased and then decreased in both test runs. This could be an indication of various properties or reactions coming into predominance as the temperature and





therefore the dispersive energy increases and it illustrates the complexity of the clay-liquid interaction.

It should be noted that some difficulties in making the volumetric readings occurred, as indicated by the variances in the test runs in the temperature bath in two instances. The difficulty was the precise reading of the meniscus of the liquid and the height of the soil. Although every effort was made for consistency in the readings, an element of doubt exists in the temperature runs because of the small variances.

#### F. Investigation of Secondary Aggregation

As discussed in Chapter III it has been observed that formation of secondary aggregations or shrinkage cracks result from water loss in the soil. As the water is lost and shrinkage occurs due to the decrease in size of the hydrate hull around the particle, tension forces are built up on the surface of the soil. Initially as the tension builds up it may be relieved by plastic flow but once the material loses this plasticity tension cracks begin to form.

From the description of this phenomena it appears that the formation of secondary aggregations might well be a function of two dependent events: the plasticity (plastic limit); and the cohesive forces between the soil particle. It would seem that with a lower plastic limit in a soil, one would expect the soil to have plastic properties in a lower moisture range. Therefore it would appear that the soil might be able to relieve the tension stresses built up during drying and shrinkage for a longer period by plastic flow. This would mean that for a lower plastic limit



one would expect less crack formation. In the case of cohesive forces it seems that with stronger forces between particles the soil would be able to resist the tension forces more easily again resulting in a lower number of shrinkage cracks.

Considering the photographs (Figs. 15-24) of the shrinkage cracks with various soils and liquids it appears that this is precisely what happens. For Bentonite and DMSO and DMF, there are a great number of shrinkage cracks while with Bentonite and water there are none. Bentonite and DMSO have a substantially higher plastic limit than do Bentonite and water. For the case of Attapulgitite and DMF and DMSO there again are a greater number of shrinkage cracks than for Attapulgitite and water. The plastic limit of Attapulgitite and DMSO is substantially greater than for Attapulgitite and water. It is important to note that in the case of Attapulgitite the plastic limits are extremely high due to the unusual tubular structure (see Section I B) of the mineral. Finally for the Kaolinite it can be seen that no shrinkage cracks occurred. This may be due to the quite low plastic limit of all the Kaolinite samples.

The small number of shrinkage cracks observed in the Attapulgitite and water and Bentonite and water also are a result of the increased cohesiveness of these materials which in part determined the low plastic limit of these mixtures. This difference in cohesiveness of the materials in organic liquids and water may further be explained by the attraction and solvation of the negative (anion type) surface with the water which does not occur in the case of the organic liquids.



#### IV. CONCLUSIONS

The results of this work seem to further emphasize the importance of physical chemical factors on the interaction of clay minerals and liquids. The data point out quite emphatically the importance of the electric and geometric properties of both the soil and liquid in determining parameters affecting the physical properties of the system as a whole. Particularly important are the electrical and geometric nature of the mineral particles and the electrical properties of the liquid including the dipole moment and dielectric constant plus the geometric structure or size and shape of the molecules composing the liquids.

The experimental work shows that in the case of the expanding lattice Bentonite and the Attapulgite the dielectric constant of the liquid coupled with the strong negative surface of the mineral and the inability of the organic liquids to solvate anion type surfaces may cause the lower apparent soil liquid interaction, i.e., the lower the dielectric constant, the lower the interaction. Also important however are the geometric properties, particularly obvious in the case of Attapulgite. The larger geometric size of the DMSO and DMF molecules seem to hinder the migration of these liquids into the unusual tubular structure of the mineral further affecting the apparent soil-liquid interaction.

In the case of the non-expanding lattice Kaolinite the experimental work indicates an increase in the soil-liquid interaction with organic liquids, the opposite effect of the expanding-lattice and Attapulgite tests. This result appears to be affected by the larger dipole moment of the organic liquids and the tendency of Kaolinite to sorb more of certain organic liquids.





The results of this work also seem to agree with previous experimentation done by Winterkorn and Bayer [23], Waidelich [20], and E. W. Russell [17]. Winterkorn and Bayer had determined in the case of expanding lattice clays that sorption decreased with the dielectric constant. Waidelich found around 1957 that the behavior of the expanding lattice clays in the consolidation test was affected by the dielectric constant while the dipole moment seemed to be the governing factor in non-expanding lattice clays. Russell found that the apparent specific gravity is affected with the use of various liquids and soil combinations.

It was unfortunate that time became a limiting factor in this work. Further verification of the results would be realized had it been possible to incorporate other organic liquids in the experimentation. Particularly useful would be additional sorption tests for Kaolinite and Attapulgite using liquids varying in electrical properties and molecular size. Also useful would be additional specific gravity tests, Atterberg limit tests and sediment volume tests with a variety of liquids. The authors also feel that additional investigation might be feasible concerning the stabilization of soil using the DMSO liquid to carry a stabilizing agent. DMF although an excellent solvent would not be useful in this respect, i.e., as a carrier because of its highly toxic properties.



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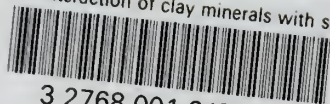






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